Reaction mechanism of solvated *n*-BuLi with thiophene in THF: A theoretical and spectroscopic study

by

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Submitted in partial fulfilment of the requirements for the degree

Master of Science

The Faculty of Natural and Agricultural Sciences

University of Pretoria

(2018)

Declaration

I, Bryan William Bulling declare that the dissertation, which I hereby submit for the degree Master of Science: Chemistry at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution. In addition, all corrections to the dissertation as agreed upon with external examiners have been done satisfactorily.

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Abstract

It is widely known that organolithium reagents, such as *n*-BuLi, play an important role in chemistry. Therefore, the role the reagent undergoes in any chemical system is an important aspect to investigate. Hence, this work originated on the prospect of better characterising the reactivity and behaviour of *n*-BuLi in an aprotic solvent.

It this theoretical study, a conformation search protocol designed for analysis of a large set of low energy conformers was implemented in order to select the lowest energy conformers (LECs) of several solvated and unsolvated species of *n*-BuLi in THF. Furthermore, the protocol was enhanced to incorporate DFT empirical dispersion to improve the accuracy of the structural geometries; they compared well with those computed at the MP2 level. The computed LECs were used to investigate the 1) oligomerisation, 2) solvent effects, 3) mixed-aggregate stabilities and 4) theoretical 1-dimensional NMR data of *n*-BuLi in THF. From these data, the different equilibrium aggregation states of *n*-BuLi were characterised at –78°C and the oligomerisation was found to be induced by the coordination of THF. The favoured and most stable dimer and tetramer *n*-BuLi species are both tetra-solvated. Following the theoretical analysis on the structural behaviour of *n*-BuLi in THF, 1-dimensional ^{1}H, ^{13}C, and ^{7}Li NMR were generated experimentally with which to compare alongside literature. A complete comparison between the data sources provided a concluding synergy confirming the reported mixed-aggregation of *n*-BuLi in THF solution.

Use of a reaction modelling protocol (involving two unique solvation models) was implemented for the full investigation into the reaction mechanism of *n*-BuLi with mono-halogenated (bromine and chlorine) thiophene in THF. The reaction analysis yielded full characterisation of the reaction energy profiles and stationary points for over twenty unique chemical reaction systems. The reaction study shows that the mechanism for which lithium–halogen exchange occurs through the formation of the ate-complex (when a Lewis acid combines with a Lewis base whereby the central atom (from the Lewis acid) increases its valence and gains a negative formal charge) as proposed in the literature. The stability of the ate-complex is dependent on how well the halogen can accommodate a negative charge and the degree of lithium interaction. Hence, bromine has favourable reactivity over chlorine as the generated TSs along the reaction energy profile are significantly more stable. This work opens up a new field in theoretical/computational studies of reaction mechanisms involving *n*-BuLi in countless organic synthetic reactions reported to-date.

Acknowledgments

Firstly, I am greatly indebted to Professor Ignacy Cukrowski, for if not for his determination and financial assistance I would not have had the grateful opportunity of studying a master's degree in chemistry. In addition, I would like to express my sincere gratitude to my supervisors Professor Ignacy Cukrowski and Doctor Darren Riley, for their constant guidance and moral support throughout the past three years. The work herein could not have been made possible without the constant help and support from my research colleagues at the University of Pretoria, thank you. I want to also express my appreciation to my parents and siblings for the constant love, financial support and advise they have offered me throughout the duration of my postgraduate studies.

Special thanks to all my friends who have accompanied me throughout this journey the past few years, most importantly, Erika M. Dresselhaus and C. Johan van der Westhuizen. They were always encouraging and supportive.

I wish to express my gratitude to the National Research Foundation of South Africa and to the University of Pretoria for financial support which enabled me to complete my studies. I would also like to acknowledge the use of the Centre for High Performance Computing (CHPC) resources in South Africa and the NMR team at the University of the Witwatersrand (WITS), which made it possible to carry-out this research.

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Abbreviations

1-D	One-Dimensional
2-D	Two-Dimensional
Add	Adduct
BLYP	Becke's and Lee, Yang and Parr's gradient-corrected correlation functional
B3LYP	Becke's three parameter hybrid exchange potential gradient-corrected correlation functional combined with Lee–Yang–Parr correlational functional
CCM	Computational Chemistry Modelling
CSM	Continuum Solvation Model
DCSM	Discrete–Continuum Solvation Model
DFT	Density Functional Theory
DFT–D	Dispersion corrected DFT
DNMR	Dynamic Nuclear Magnetic Resonance
D_2O	Deuterated Water
EPR	Electron Paramagnetic Resonance
GC	Gas Chromatography
GD3	Grimme's empirical dispersion correction model
GIAO	Gauge-Independent Atomic Orbital
HF	Hartree-Fock
HSM	Hybrid Solvation Model
IRC	Intrinsic Reaction Coordinate
LDA	Lithium diisopropylamide
LEC	Lowest Energy Conformer
LiBr	Lithium Bromide
LiCl	Lithium Chloride
LUMO	Lowest Unoccupied Molecular Orbital

MM	Molecular Mechanics
MMFF	Molecular Mechanics Force Field
MP	Møller–Plesset Pertubation Theory
MP1	Møller–Plesset first-order
MP2	Møller–Plesset second-order
n-BuLi	*n*-Butyllithium
NMR	Nuclear Magnetic Resonance
PCM	Polarizable Continuum Model
PES	Potential Energy Surface
Prod	Product
QM	Quantum Mechanical/Mechanics
RB3LYP	Restricted B3LYP
React	Reactant
RINMR	Rapid Injection Nuclear Magnetic Resonance
SET	Single electron transfer
SCF	Self-Consistent Field
STQN	Synchronous Transit-Guided Quasi-Newton
THF	Tetrahydrofuran
THF–d_8	Deuterated THF
TMEDA	Tetra–methylethylenediamine
TS	Transition State
UB3LYP	Unrestricted B3LYP
ZPVE	Zero Point Vibrational Energy

Chapter 1

Introduction

1.1. Background information

The earliest known prepared organometallic compound was by 18th century French chemist Louis–Claude Cadet de Gassicourt, who without ever knowing, synthesized cacodyl [$C_4H_{12}As_2$] while conducting his work on invisible ink.[1] Since then considerable progress has been made in the structural and chemical characterisation of organometallic compounds and notably led to Nobel prized works such as those by Fischer *et al* and Chauvin *et al*, on metallocenes and alkene metathesis, respectively.[2,3] Organometallic compounds are directly characterized by the formation of polar bonds [$M^{\delta-}$—$C^{\delta+}$] between the metal and carbon atoms. This lucid bond characterization makes organometallic compounds relatively stable and reactive in solution, hence serving as functional synthetic intermediates and catalysts in industry.[4,5]

The alkali–metal organometallic (organoalkali–metal) reagents are widely used in organic synthesis and have often been utilised as analogues to Grignard reagents. To date, organometallics have surpassed Grignard reagents owing to increased applications, synthetic yields and reaction rates. Important alkali–metal–containing organometallics are the organolithium reagents [$R^{\delta-}$—$L^{\delta+}$], which have been extensively studied since the 1930s, with Wittig and Gilman being credited with their discovery.[6–8] Predominantly, organolithium reagents are utilised for either oxidative addition or exchange reaction paths. The latter is more ubiquitous in the synthesis and one of the primary exchange reaction methods is direct metalation.[9] Metalation is a common reaction technique for generating organolithium compounds by exchange of a reactive hydrogen species. This method involves acid–base equilibria, with the replacement of a hydrogen [H] by an alkali metal [M**]** favouring the products with increasing acidity (larger pK_a) of R^1—H (equation 1.1).

$$R\text{—}M + R^1\text{—}H \rightleftharpoons R\text{—}H + R^1\text{—}M \tag{1.1}$$

Though the product lies on the side of the weaker acid, the acidity of R^1—M compared to R—H is not a true measure for the reactivity and chemical kinetics. One synthetic example is the chemical reaction of benzene (stronger acid) and *n*–butyllithium (*n*-BuLi), yielding butane (weaker acid) and phenyl–lithium. The chemical reaction unassisted is immeasurably slow, but rapid metalation occurs when the co–solvent tetra–methylethylenediamine (TMEDA) is introduced. This behaviour is explained by the complexation of Li^+ with the strong σ-donor TMEDA, consequently, the polarisation of the Li—C bond is amended, hence the increased reactivity of the characteristic carbanion on the butyl group.[3]

Metal–halogen exchange (lithium–halogen exchange), an alternative exchange reaction method, is well–known and most commonly used as a synthetic tool for generating organolithium reagents.[8] The reaction system for metal-halogen exchange involves the equilibrium shifted to the right if R^1 is superior to R in stabilizing a negative charge (equation 1.2).[5]

$$R—M + R^1—X \rightleftharpoons R—X + R^1—M \qquad (1.2)$$

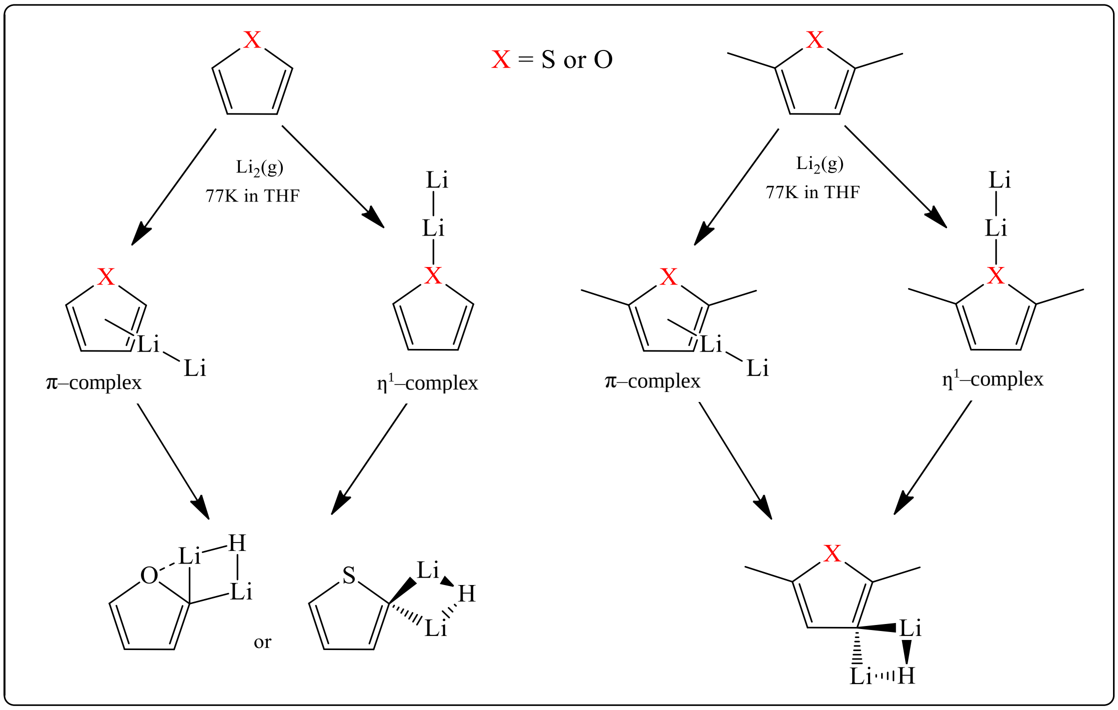
Aromatic aryl halides are commonly used reagents due to the inherent stabilisation of charge and thus, studies on metal-halogen exchange have generated an order of reactivity for the halogens atoms; I > Br > Cl >> F. Furthermore, the exchange reaction is relatively spontaneous and is handled at low temperatures for both kinetic control and to prevent by–product formation (organometallic reactivity with substrate/solvent). [5,7]

Mechanistic studies on exchange reaction methods with lithium are among the earliest to be reported, notably because of their considerable use in chemistry. Though extensively published, the mechanism/s involving lithium reagents is still a debated topic. [4-14] Experimental findings have found that most lithium reagents in fact exist and react as oligomers/mixed-aggregates.[4-11] In addition, such species in solution may undergo intermediate changes,[14] such as halogen–dancing.[15,16] The most relevant observation is the degree of aggregation, which is primarily dependent on the solvent/co-solvent. Kinetic and NMR studies show that the reaction rate of the organolithium reagent decreases as the aggregation advances; monomer > dimer > tetramer > hexamer.[10]

The complexity of an organolithium mechanistic system is due to complicated structures which are sensitive to reactivity in response to solvent, temperature, the formation of aggregates, etc. This suggests that it is necessary to gain additional insight, preferably at a molecular level. This may be achieved by the implementation of theoretical computational chemistry, which has been regarded as an operable instrument for investigating chemical reaction mechanisms.[17-19] The study requires the selection of an appropriate substrate, organolithium reagent and solvent environment with which to subject to inexorable computational chemistry for mechanistic investigation. *n*-BuLi along with lithium diisopropylamide (LDA) are the preferred reagents selected due to being regularly used in synthesis and being readily available. The solvents typically used for organolithium reactions are polar aprotic in nature and examples of these are tetrahydrofuran (THF), diethyl ether and occasionally the co–solvent TMEDA. Thiophene was selected as the appropriate reactant to conduct lithium-exchange with as it is known to be stable and easy to model.[19,20] Additionally, this allows the possibility to study the effects of aromaticity and heteroatoms on the anion stabilities relating to organolithium synthesis. Our interest purely lies in the scope of organolithium exchange reactions and the mechanistic theoretical study using computational chemistry.

1.2. Mechanistic Scheme: Metalation

Experimentally, the exchange reaction of metalation is determined by the acid-base equilibria correlating to deprotonation and exchange occurring at the most acidic site, which is typically the α–position to the heteroatom, as is the case with thiophene.[21] Computationally, a gas phase theoretical study by Mendoza *et al*,[22] illustrates the metalation of thiophene and analogue derivatives, Scheme 1.1.



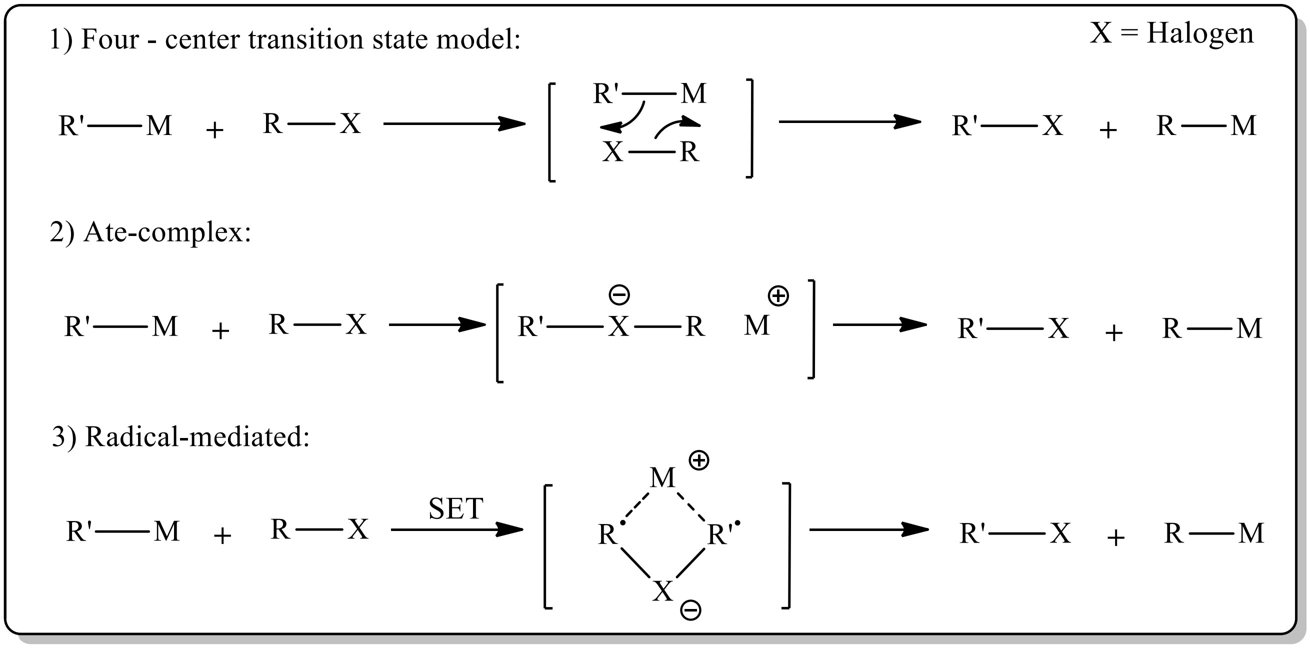
Scheme 1.1. Theoretically predicted coordination modes of metalation intermediates by Mendoza *et al*.[22]

In the study, it was found that metalation involves at least two steps, first an intermediate coordination of the di-lithium (Li_2) cluster with the aromatic compound, followed by insertion of the Li_2 into the C—H bond. For the intermediate step, it is understood that there are two different possibilities for a di–lithium cluster Li_2(g) to coordinate to the heteroatoms, by forming either a π– or η^1–complex as shown in Scheme 1.1.

For furan, the study showed that the preferred pathway intermediate is via the η^1-complex and for thiophene, the favoured pathway is via the π–complex. From the experimental section, no metallation occurs for pyrrole (X = N) due to the LUMO energy being considerably higher compared to furan and thiophene, therefore resulting in no C—H activation.[22] There are numerous experimental and kinetic studies investigating metalation reactions and their mechanisms with different reaction conditions,[10,11] however, little has been done on exploring the mechanism of metalation in solution using computational chemistry.

1.3. Mechanistic scheme: Metal-halogen exchange

Despite its importance in the synthesis of organolithium reagents, the mechanism of metal-halogen exchange is not yet fully understood, as is the same for many organometallic processes.[23] Though the true mechanism is still debatable, there have been various studies to date that have proposed general intermediate/transition state postulates.[6,7,10,23] Referring to Scheme 1.2, there is the four-centred transition state reaction, the formation of an ate-complex (10–X–2 ate complex) intermediate and a stepwise process (radical mediated mechanism) initiated by a single electron transfer (SET).



Scheme 1.2. Proposed in the literature mechanistic schemes for halogen–metal exchange.

The four–centred transition model has been noted as being the least likely to explain the mechanism but is a rather good description of the exchange reaction. The ate complex mechanistic intermediate, was suggested by Wittig,[24] and it is explained by the nucleophilic attack of R—Li at

$R^{'}$—X resulting in the formation of a bridging halogen.[6] Experimental studies over the years have supported the formation of ate-complex intermediates,[6,10–12,23,25] one such discovery supporting the mechanistic scheme, was the X–ray crystallographic analysis of isolated $[C_6F_5—I—C_6F_5]^{-}$ (Li^{+}·2TMEDA) at room temperature.[25] A Theoretical study by Wiberg *et al*,[26,27] focused on the solvation and structural effect of ate-complexes derived from the reaction of alkyllithiums and aryllithiums, with the corresponding organohalides. Furthermore, they managed to a high degree of accuracy to reproduce the experimental results for the formation of $[C_6F_5—I—C_6F_5]^{-}$ (Li^{+}·2TMEDA),[25] hence demonstrating that computational modelling is viable for studying such systems. The latter radical-mediated mechanistic scheme proposes the intermediate formation of radicals in a solvent cage. The exchange reaction involving radical species is initiated by a single-electron-transfer step (SET).[6] Evidence for radicals has been commonly studied through the use of radical clocks and probes assisted with detection of intermediates using UV, NMR, electron paramagnetic resonance (EPR) and even gas chromatography (GC).[5,6,12,14] Although studies demonstrate that radical behaviour is observed for the reactions between organolithiums and organohalides, it in no way proves the existence of a radical cage where radicals are involved intermediates.

This concludes that the mechanism for metal–halogen exchange is still unresolved and there may ultimately be an overriding mechanism at play that leads to different experimental observations. For the latter two mechanistic schemes, theoretical studies via computational chemistry have been conducted for numerous reaction systems involving lithium exchange; however, as previously mentioned the mechanism is ambiguous.[7,10-12,23,26-29]

1.4. Aggregates and NMR

The first single-crystal X-ray structure obtained of a lithium reagent was ethyllithium in 1963 resembling a cubic–tetramer crystal lattice.[30] One year later, the methyllithium crystal structure was reported.[31] To date, the number of reported solid-state organolithium structures extending from monomeric to polymeric is immense.[11] Of these, there is a reported solid-state structure of *n*-BuLi determined by X–ray crystallography for the tetra-solvated tetramer [*n*-BuLi·THF]$_4$ in hexane, bi-solvated dimer [*n*-BuLi·TMEDA]$_2$ and pure *n*-BuLi oligomer in hexamer [*n*-BuLi]$_6$.[32,33] The former *n*-BuLi crystal structure exhibits a distorted tetramer with each lithium cation bonded to three separate *n*-BuLi α-carbons and solvated by one THF molecule, see Figure 1.1. The *n*-BuLi hexamer was reported to be unique as the β–C atoms are arranged in such a way, as to suggest interaction with the Li atoms.

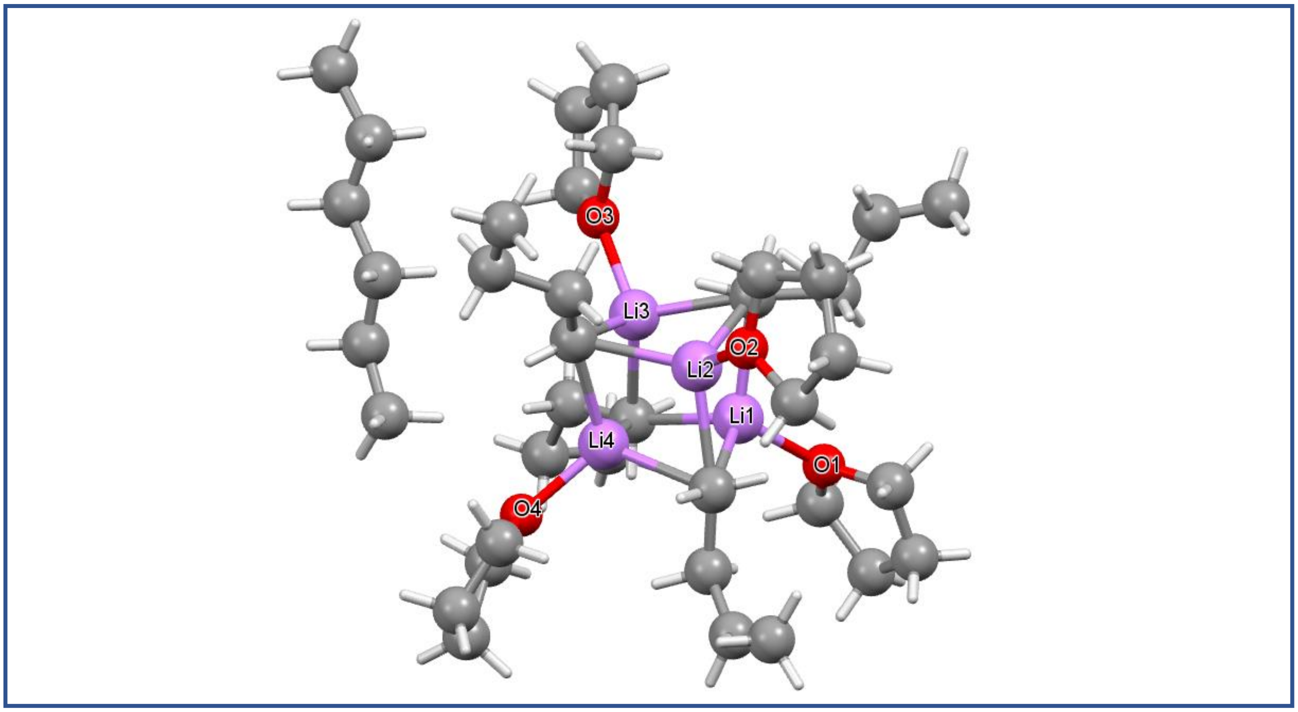
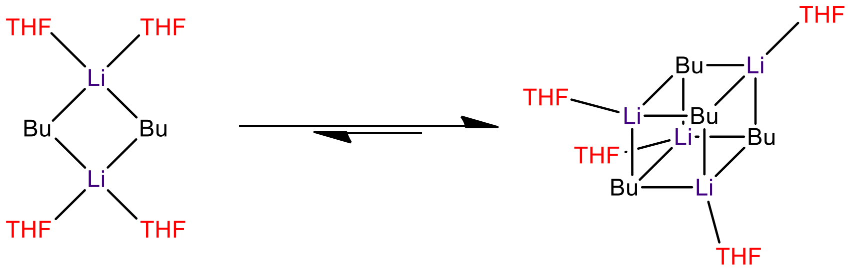


Figure 1.1. The crystallographic structure of [*n*-BuLi·THF]$_4$, obtained in *n*-hexane, CSD–WAFJES.[32].

From the experimental findings and crystal structures, it was believed that the structure of organolithium reagents in solution (liquid phase) resembles that of the solid-state phase. This postulation led many studies into using various experimental techniques to validate and confirm the existence and extent of aggregation in solution.

Early experimental methods involved the use of cryoscopy (freezing point depression) and ebullioscopy (boiling point elevation).[34] Though characterisation of such structures in solution is intrinsically less precise, the early experimental findings supported the notion that aggregates exist in solution. Later the use of low temperature NMR spectroscopy, integrating kinetic studies and 2-dimensional techniques, provided the supporting evidence for the existence of aggregates and characterisation of the solvent-state structure.[10,11,35–41] Furthermore, it is deduced that the nature of aggregation is strongly dependant on the basicity of the solvent and of the carbanion. In the case of *n*-BuLi, the structure is reported as a mixed aggregate tetramer/hexamer in less basic hexane.[5,10] In the presence of basic THF, *n*-BuLi dissociates into a mixed-aggregate of tetra-solvated tetramer (major species) in equilibrium with a tetra-solvated dimer, see Figure 1.2. The dissociation is probably due to the coordination of aprotic solvent.[10,35,39–41] The nature of co-existing mixed-aggregates in solution is not limited to *n*-BuLi or simple alkyllithiums but is also observed for allyllithiums, aryllithiums, vinyllithiums and many more functional groups.[11]

Experimental kinetic works conducted for phenyllithium (monomer/dimer) and *n*-BuLi using rapid injection NMR (RINMR) and dynamic NMR (DNMR), have reported the barrier (activation energy) of lithium mixed-aggregate species interconversion. For *n*-BuLi, the species interconversion free energy is reported as approximately $\Delta G^{\ddagger}$ = ~10.3 kcal mol^{-1}.[10,35,40]



$$2(n\text{-BuLi})_2\cdot 4\text{THF} \rightleftharpoons (n\text{-BuLi})_4\cdot 4\text{THF} + 4\text{THF}$$

Figure 1.2. The mixed-aggregate species interconversion of *n*-BuLi in THF.[35-41]

The tetra-solvated dimer is reported as primarily the reactive aggregate, far more active than the tetramer. Therefore, synthesis using *n*-BuLi largely involves the dissociation of the tetramer/hexamer aggregate mixture of *n*-BuLi in hexane (commercial solution) into the active dimer when THF is present. The process of dissociation is reported to be complete within 10 ms at temperatures below –78 °C.[10] The identical de-aggregation behaviour is observed for the co-solvent TMEDA and analogues.[11,41]

1.5. Aim of the Project

The chapters to follow, involve primarily a theoretical investigation into the solvated-state structures and reactivity of *n*-BuLi with halogenated thiophene in the presence of THF. It is anticipated that this study may add theoretical synergy to the current experimental knowledge relating to the mechanistic behaviour of organolithium reagents, especially since organolithium reagents have industrial applications as initiators for chain-growth polymerization,[42] and are functional in pharmaceutical asymmetric synthesis development.[43]

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Chapter 2

Computational Methods

2.1. Introduction

Computational Chemistry Modelling (CCM), is a field of study explored through curiosity and only limited by one's imagination and dedication. CCM has been extensively developed over the past few decades as an adjunct to experimental work and is driven by the need to explore the physical realm of atoms and the infinite molecular structures thereof. CCM is a tool used to attempt to comprehend problems that scientists observe every day, by computing a chemical reality through which studying the behaviour of physical systems utilising the fundamental laws of physics. The modelling methods implemented for studying the physical properties of a system, belong to two broad classes: molecular mechanics and electron structural theory. Both perform the basic type of calculations, but they differ based on the physical laws used; molecular mechanics applies classical mechanics (Newtonian mechanics) and electron structural theory applies quantum mechanics. The subsequent output and central concept of CCM is the study of the potential energy surface (PES). This is the graphical or mathematical relationship between both the energy and geometry of the molecular system.[1,2]

CCM is perceived as a necessary instrument in modern chemistry, due to the abundant theoretical models developed over the years.[1-5] The applications for modelling are numerous, which include molecular structure prediction (spatial arrangement), relative system energies, electronic density distribution, vibrational frequencies for reproducing experimental spectra, reactivity and transition state analysis for chemical reactions and so forth.

This Chapter focuses on explaining briefly the theoretical background of each method used and various aspects of CCM. The theoretical work presented in this chapter is derived from the following sources on CCM; *Exploring Chemistry with Electronic Methods (2nd edition)* by Foresman and Frisch[1] and *Computational Chemistry; Introduction to the theory and applications of Molecular Quantum Mechanics* by Errol G. Lewars.[2]

2.2. Molecular Mechanics

Molecular mechanics (MM) is based on a ball-and-spring model for molecules. Rooted in the laws of classical physics (also known as Newtonian mechanics) to predict the structures and properties of molecular systems. A chemical system simulated in molecular modelling can be explored with various molecular mechanic methods. Each method can be defined by a particular force field (not to be confused with a force field in classical physics). A force field is a set of energy functions and parameters used to predict and calculate the potential energy of a molecular system that depends on the position of its constituent atoms and environment for each atom type.

Parameters (chemical bonds, torsion angles, etc.) used in the energy functions are generally empirical by means of experimental studies. In MM theory, the potential energy changes as the geometry changes and is a function defined by the sum of the bonded and nonbonded interactions, as written:

$$E_{Total} = \sum E_{Bonded} + \sum E_{Nonbonded} \tag{2.1}$$

Bonded and nonbonded terms refer to the respective covalent (bond, angle and dihedral) and noncovalent (van der Walls and electrostatic) interactions between atoms.

$$E_{Bonded} = \sum E_{Bonds} + \sum E_{Angles} + \sum E_{Dihedrals} \tag{2.2}$$

$$E_{Nonbonded} = \sum E_{vanderWaal} + \sum E_{Electrostatic} \tag{2.3}$$

The basic understanding of molecular mechanics is the expression of the energy, which as a function is defined by the molecules structures ability to resist stretching, bending and strain. This, in turn, is used to determine properties such as bond lengths, dihedral angels and energy minimum (PES minima, $\partial E / \partial q = 0$ for all of q, q is a geometric parameter).

With MM methods, the ∂potential energy of a definite molecule with a plausible geometry can be approximated. The input structure is then varied along the potential energy surface (geometry optimisation) until convergence to a structure where the forces of the system are equal to zero (stationary point). MM calculations are inexpensive computationally and it is therefore possible to perform modelling for large systems (thousands of atoms, such as proteins) since the method essentially only equates for nuclei interactions (Born-Opperheimer approximation: nuclei in a molecule are stationary relative to the electrons). The electronic effect of all electrons is only added somewhat implicitly into the applied force field. Molecular mechanics cannot report on electronic spectra nor define energies and shape of molecular orbitals. Therefore, the lack of electronic interactions implies that the MM method is limited to several classes of molecules and that the force field can only achieve good results for the systems it has been parameterised. Without electronic effects, systems involving bond formation and dissociation cannot be described and the electronic properties of molecular systems are therefore not reproducible.

Most frequently, MM is used to obtain conformational structures (geometries) resembling a desired stationary point which serves as an input for electronic structural methods such as *ab* *initio*, semi-empirical, or density functional theory calculations. This was also emphasized in mywork, which was published in 2016.[6]

2.3. Electronic Structure Methods

The basis of electronic structural methods in computational chemistry is the use of quantum mechanics which states that the energy and molecular properties are related to solving the time-independent Schrödinger equation:

$$\hat{H}\,\Psi = E\,\Psi \tag{2.4}$$

where $\hat{H}$ is the Hamiltonian operator, Ψ is the wavefunction and E is the energy of the system. Solving the true Schrödinger equation for most systems is impractical, even with modern computational power. In order to mathematically derive the equation effectively, approximations are to be made (i.e. Born-Oppenheimer). Therefore, the different electronic structure methods are characterised by their mathematical approximations for deriving the Schrödinger equation. The three broad classes of electronic structure methods are semi-empirical, *ab initio* and density functional theory (DFT), of which *ab initio* and DFT will be discussed in the following sections.

2.4. *Ab initio* methods

Ab initio methods, use mathematical approximations, physical constants and the principal laws of quantum mechanics to solve the Schrödinger equation. Unlike molecular mechanics and semi-empirical methods, no experimental parameters are used. This implies that *ab initio* methods are not limited to any molecular system and generally produce excellent quantitative results, but, at the cost of computational time. It depends purely on solving the Schrödinger equation to characterise a molecular system. So, before we discuss some of the commonly used *ab initio* methods, it is important to define the Hamiltonian operator which acts on the wavefunction and corresponds to the total energy of the system.

For a molecular system, Ψ is the function for the spatial arrangement of the electrons (r_i) and nuclei (R_i) within the molecule. The Hamiltonian in the classical sense is made up of both the kinetic ($\hat{T}$) and potential ($\hat{V}$) energy terms of a system in the form:

$$\hat{H} = \hat{T} + \hat{V} \tag{2.5}$$

The kinetic energy term can be subdivided into the sum of both the electronic $(\hat{T}_e)$ and nuclei $(\hat{T}_n)$ energies. For the potential energy term, we can represent the components as the Coulomb repulsion and attraction between each pair of charged entities. Therefore, the full Hamiltonian for the molecular system can be written as:

$$\hat{H} = \hat{T}_e(\vec{r}) + \hat{T}_N(\vec{R}) + \hat{V}^{Ne}(\vec{R},\vec{r}) + \hat{V}^{ee}(\vec{r}) + \hat{V}^{NN}(\vec{R}) \tag{2.6}$$

the potential energy terms ($\hat{V}^{Ne}, \hat{V}^{ee}, \hat{V}^{NN}$) correspond to the Coulombic nuclear-electron attraction, electron-electron repulsion and nuclear-nuclear repulsion, respectively. Since *ab initio* methods involve the use of mathematical approximations to simplify the Schrödinger equation, it would be informative to talk about the most commonly used Born-Oppenheimer approximation. The approximation separates the electron and nuclear motions, by noting that the nuclei move slowly in comparison to the electrons. This therefore means the electron distribution within a molecular system depends primarily on the spatial arrangement of the nuclei, and not on their velocities. Thus, an electronic Hamiltonian can be constructed which is easier to derive since the kinetic energy term $\hat{T}_N(\vec{R})$ is disregarded:

$$\hat{H} = \hat{T}_e(\vec{r}) + \hat{V}^{Ne}(\vec{R},\vec{r}) + \hat{V}^{ee}(\vec{r}) + \hat{V}^{NN}(\vec{R}) \tag{2.7}$$

For the rest of the methodology, it is assumed the Born-Oppenheimer approximation to be in effect.

For each *ab initio* method, various approximations are used. Thus, if fewer approximations are made to the Schrödinger equation, we generally get an increase in accuracy with an increase in cost. So, for any molecular system and research problem, determining the right electronic structure method to implement is important. In this work, we worked with the Møller–Plesset Pertubation Theory (MP). MP is built on the *ab initio* method known as Hartree-Fock (HF)which is relevant to discuss.

2.4.1. Hartree-Fock Method

Hartree-Fock is the simplest of the *ab initio* calculations and was designed and performed on atoms by Hartree in 1928. It was designed to address the problem of determining the exact solution of the Schrödinger equation, where for many-electron systems it was not possible. So, with a number a simplifying assumptions and procedures an approximate numerical solution was possible. The HF method is synonymous with the molecular orbital approximation to define the wavefunction for each electron in the molecular system. The wavefunction is made up of a combination of molecular orbitals (ϕ_1, ϕ_2,….)and so a normalised set of orthogonal orbitals is selected:

$$\iiint \phi_i^* \phi_i \, dx \, dy \, dz = 1$$

$$\iiint \phi_i^* \phi_j \, dx \, dy \, dz = 0; \quad \mathrm{i} \neq \mathrm{j} \tag{2.8}$$

Therefore, the wavefunction as a combination of molecular orbitals is written as:

$$\psi(\vec{r}) = \phi_1(\vec{r}_1)\ \phi_2(\vec{r}_2) \ldots \phi_n(\vec{r}_n) \tag{2.9}$$

However, such a wavefunction is not antisymmetric (function must change sign when two identical particles are interchanged $f(i,j) = -f(i,j)$). The simplest antisymmetric wavefunction that is a combination of molecular orbitals (ϕ_1, ϕ_2,….) is known as a Slater determinant (Φ_{SD}). The determinant, unlike equation 2.9 needs to account for doubly occupied orbitals and electron spin (electron can have spin up +1/2 or spin down –1/2). Most computational calculations use the closed shell system (Restricted Hartree-Fock) whereby each orbital is accompanied by a pair of electrons of opposite spin. The two spin functions, α and β with the closed shell limit are defined as:

$$\alpha(\uparrow) = 1 \qquad \alpha(\downarrow) = 0$$

$$\beta(\uparrow) = 0 \qquad \beta(\downarrow) = 1 \tag{2.10}$$

The product of molecular orbital and electron spin functions α and β, will define the overall electronic wavefunction ψ and produce spin orbitals (Note. Spin orbitals are orthonormal since the orthogonal molecular orbitals were normalised). Now that electron spin has been accommodated into the closed shell wavefunction, one can then express the Slater determinate by using $^{N}\!/_{2}$ molecular orbitals with N electrons with opposite spin:

$$\psi(\vec{r}) \approx \Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1)\alpha(1) & \phi_1(\vec{\mathrm{r}}_1)\beta(1) & \phi_2(\vec{r}_1)\alpha(1) & \phi_2(\vec{\mathrm{r}}_1)\beta(1) & \cdots & \phi_{N/2}(\vec{r}_1)\alpha(1) & \phi_{N/2}(\vec{\mathrm{r}}_1)\beta(1) \\ \phi_1(\vec{r}_2)\alpha(2) & \phi_1(\vec{\mathrm{r}}_2)\beta(2) & \phi_2(\vec{r}_2)\alpha(2) & \phi_2(\vec{\mathrm{r}}_2)\beta(2) & \cdots & \phi_{N/2}(\vec{r}_2)\alpha(2) & \phi_{N/2}(\vec{\mathrm{r}}_2)\beta(2) \\ \vdots & \vdots & & & & & \\ \phi_1(\vec{r}_N)\alpha(\mathrm{N}) & \phi_1(\vec{\mathrm{r}}_2)\beta(\mathrm{N}) & \phi_2(\vec{r}_\mathrm{N})\alpha(\mathrm{N}) & \phi_2(\vec{\mathrm{r}}_2)\beta(\mathrm{N}) & \cdots & \phi_{N/2}(\vec{r}_\mathrm{N})\alpha(\mathrm{N}) & \phi_{N/2}(\vec{\mathrm{r}}_\mathrm{N})\beta(\mathrm{N}) \end{vmatrix} \tag{2.11}$$

The Slater determinate formulation preserves the antisymmetric wavefunction, as swopping two electrons corresponds to interchanging two rows of the determinate and a change in sign. These determinate mixes all possible spin orbitals for all electrons in the system and considers all possible electron locations (probability density) to generate the wavefunction.

The next approximation used in HF involves defining the molecular orbitals as basis functions. This involves expressing the orbitals as a linear combination of pre-defined one electron functions. Basis function resemble atomic orbitals centred on atomic nuclei, and therefore the sum of atomic orbitals generates molecular orbitals as expressed:

$$\phi_1 = \sum_{\mu=1}^{N} c_{\mu i}\chi_{\mu} \tag{2.12}$$

where $c_{\mu i}$ is known as the molecular orbital expansion coefficients and χ_μ the basis functions $\chi_1 \cdots \chi_N$ (Note that the basis functions are to be normalised). Now the problem arises for solving the set of molecular orbital expansion coefficients. One way of solving for $c_{\mu i}$ is the use of the variation principal. The variation principal articulates that the ground state (denoted Ξ) for any function (antisymmetric and normalised) of the electronic coordinates, the energy of the exact wavefunction is lower than that of the energy calculated for Ξ:

$$E(\Xi) > E(\psi) \qquad \Xi \neq \Psi \tag{2.13}$$

Roothaan and Hall[7] derived an equation describing the molecular orbital expansion coefficients:

$$\sum_{\nu=1}^{N}(F_{\mu\nu} - \varepsilon_i S_{\mu\nu})c_{\nu i} = 0 \qquad \mu = 1,2,\mathrm{K}\,,N \tag{2.14}$$

which can be rewritten as:

$$FC = SC\varepsilon \tag{2.15}$$

Equation 2.15 is the matrix form of equation 2.14 whereby each element is a matrix (array). The term ε is known as a diagonal matrix of the orbital energies, where each element ε_i corresponds to the one-electron orbital energy of each molecular orbital. The Fock matrix (F), represents the average effects of the field of all electrons on each molecular orbital χ_i. The S matrix is better known as the overlap matrix, which is for when orbitals overlap. The repetitive procedure for solving equation 2.15 is known as the Self-Consistent Field (SCF) method.

Hartree-Fock method provides a reasonable accuracy for geometry prediction and parameters for many molecular systems and is relatively computationally inexpensive. Though HF is a good *ab initio* base-level method, it does have limitations. One major limitation of HF is it neglects electron correlation which is the energy contribution arising from electron-electron interaction (HF does include some correlation effect but only for electrons with the same spin). For our system in this work, full electron correlation is required for deriving the optimal geometry of the molecules and modelling the chemical reactions which involve bond dissociation. One of the many post SCF methods that succeed HF and includes electron correlation for this work is discussed next.

2.4.2. Møller-Plesset Pertubation Theory

The MP method is one of the ways that is least expensive on improving Hartree-Fock. It is known as an electron correlation method as it goes beyond SCF to include electron–electron interactions, especially that of electrons with opposite spin. MP treatment of electron correlation is based on perturbation theory, whereby if one knows how to treat a simple system, then a more complex system can be mathematically treated as a modified version of the former simple system. Perturbation theory is based upon dividing the Hamiltonian as follows:

$$\hat{H} = H_0 + \lambda \hat{V} \tag{2.16}$$

H_0 has an exact solution from HF and $\lambda\hat{V}$ is a perturbation correction applied to H_0 which is assumed to be small ($\hat{V}$ is a perturbation operator and not related to the potential energy). The assumption for $\hat{V}$ would propose the perturbed wavefunction and energy can be expressed as a power series in $\hat{V}$ in terms of the parameter λ:

$$\psi = \psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \lambda^3\psi^{(3)} + ... + \lambda^n\psi^{(n)}$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + ... + \lambda^n E^{(n)} \tag{2.17}$$

$\psi^{(0)}$ and $E^{(0)}$ are the HF wavefunction and energy, respectively. Substituting the above equations 2.16 and 2.17 into the Schrödinger equation gives:

$$(H_0 + \lambda V)(\psi^{(0)} + \lambda\psi^{(1)} + ... + \lambda^n\psi^{(n)}) = (E^{(0)} + \lambda E^{(1)} + ... + \lambda^n\psi^{(n)})(\psi^{(0)} + \lambda\psi^{(1)} + ... + \lambda^n\psi^{(n)}) \tag{2.18}$$

From equation 2.18 we can equate the coefficients on either side of the equation for each power of λ, where n power of λ represents successively the higher order of perturbation (MPn). Here are the first three equations, corresponding to powers of 0, 1, 2 of λ:

$$(H^0 - E^{(0)})\psi^{(0)} = 0$$
$$(H^0 - E^{(0)})\psi^{(1)} = (E^{(1)} - V)\psi^{(0)}$$
$$(H^0 - E^{(0)})\psi^{(2)} = (E^{(1)} - V)\psi^{(1)} + E^{(2)}\psi^{(0)} \qquad (2.19)$$

Now that the general perturbation theory has been derived, the term is defined as the sum of one-electron Fock operators:

$$H_0 = \sum_i F^i \qquad (2.20)$$

The process involves solving for each energy value, E^0, $E^{(1)}$,…, $E^{(n)}$ using the expanded coefficients for n power of λ where the energy of Hartree-Fock is equivalent to MP1 energy:

$$E_{HF} = E^{(0)} + E^{(1)} \qquad (2.21)$$

For subsequent orders of λ^n it is possible to determine higher order perturbation which represents the lowering of energy, by allowing the electrons to avoid one another better than in HF. In this work, the second order perturbation MP2 is used as it is the first ‘real’ Møller–Plesset level to greatly improve on Hartree-Fock. MP2 requires ample computational resource and in this work, it was used as a tool for determining most favourable geometries of molecular structures. For modelling, chemical reactions, a more commonly used method which rivals post-SCF methods was used which is discussed in the next section.

2.5. Density Functional Theory

Density functional theory (DFT), unlike ab initio methods, is not based on the wavefunction, but rather on modelling the electron correlation via functionals (a function of a function) of the electron probability density (electron density ρ). The theory is derived from the Hohenberg-Kohn theorems,[8] which essentially state that the properties of any ground-state atom or many-body systems is obtained from the unique functional of the electron density and that the functional that determines the ground state energy of the system, must yield an energy that is greater than or equal to the true ground state energy. DFT methods have become the most popular electronic structure methods used in computational chemistry for numerous reasons. Firstly, electron density can be measured experimentally (X-ray or electron diffraction) in contrast to the wavefunction which is not a measurable feature. It is a function of position for three variables (x, y, z), whereas the wavefunction for an n–electron molecule, is a function of $4n$ variables (three spatial x,y,z and spin, for each electron). DFT includes electron correlation effects and lastly achieves qualitative results resembling expensive *ab initio* methods at essentially HF cost. Although DFT is revolutionary, the method is criticised for handling long-range van der Waal's interactions poorly (dispersion of electrons) and is primarily a ground-state theory, hence applying it to excited state systems may be precarious. Despite the shortcomings of DFT, the method is ideal for large molecular systems and new functionals may be developed to address these inaccuracies of DFT.

The approximate functionals employed by DFT methods subdivide the electronic energy term as follows:

$$E = E_T + E_V + E_J + E_{XC} \tag{2.22}$$

where E_T represents the kinetic energy, E_V is the potential energy term which includes both nuclear-electron attraction and nuclear-nuclear repulsion. E_J is the electron-electron repulsion term and E_{XC} is the exchange-correlation term for energy contribution derived from the electron-electron interaction. All electron energy terms, except for the nuclear-nuclear repulsion forming part of E_V, are functions of the electron density,ρ. The first three terms are the classical energy contributions of the electron probability density, while the last term accounts for both the exchange energy due to antisymmetry of the wavefunction and the dynamic correlation in the motions of the individual electrons. The E_{XC} is determined by the electron density and is usually approximated as follows:

$$E_{XC}(\rho) = \int f(\rho_\alpha(\vec{r}), \rho_\beta(\vec{r}), \nabla\rho_\alpha(\vec{r}), \nabla\rho_\beta(\vec{r})\, d^3\vec{r} \tag{2.23}$$

Here $\rho_\alpha$and ρ_β refer to the α and β spin density respectively. $\nabla\rho$ refers to the gradient of the total energy density. E_{XC} can essentially be separated into two parts, accounting for the different forms of electron interactions. The exchange and correlation parts represent the same-spin and mixed spin interactions respectively:

$$E_{XC}(\rho) = E^X(\rho) + E^C(\rho) \tag{2.24}$$

Both terms in equation 2.24 are functionals of the electron density and for both terms E^X and E^C the functionals are dubbed exchange functionals and correlation functionals, respectively. For each component E^X and E^C, we can either represent the functionals as a local functional (depends only on ρ) or a gradient-corrected functional (depends on both ρ and the gradient, $\nabla\rho$). For example, the local exchange functional (E^X a function of ρ) for exchange uses the simplest local density approximation (LDA) and is virtually always defined as follows:

$$E_{LDA}^{X} = -\frac{3}{2}\left(\frac{3}{4\pi}\right)^{1/3}\int \rho^{4/3} d^3\vec{r} \tag{2.25}$$

where ρ is certainly a function of r. Equation 2.25 was found to have certain flaws for defining a system and so the exchange and correlation functionals were improved upon using gradient-corrected functionals. Most current DFT methods are defined by pairing the gradient-corrected exchange functional along with the gradient-corrected correlation exchange functional. Two well-known examples (termed BLYP) are Becke's [9] and Lee, Yang and Parr's [10] gradient-corrected correlation functional. Here is an example of a gradient-corrected exchange functional based on LDA:

$$E_{Becke88}^{X} = E_{LDA}^{X} - \gamma\int \frac{\rho^{4/3}x^2}{(1+6\sinh^{-1}x)} d^3\vec{r} \tag{2.26}$$

where $x = \rho^{-4/3}|\nabla\rho|$ and γ is, a parameter chosen to fit the known exchange energies of the system.

Following the gradient-corrected functionals, another improvement was made by the addition of the Hartree-Fock exchange term. These are termed hybrid functionals as they formulated functionals which include an exchange functional which is a mixture of HF and DFT and a DFT correlated functional. The hybrid exchange-correlation functional is defined as:

$$E_{hybrid}^{XC} = c_{HF}E_{HF}^{X} + c_{DFT}E_{DFT}^{XC} \tag{2.27}$$

The first successful hybrid method was the Becke-style three-parameter functional known as B3LYP. B3LYP is a very popular method and is reported to be durable and reliable for calculating qualitative properties for various molecular systems, [3,5] including Li-containing systems such as those found in this study [11a-c]. B3LYP is used predominately to model the geometric structures, chemical properties and reactions.

2.6. Solvation and Dispersion effects

2.6.1. Solvation

Solvation effects are an important feature to consider for any molecular system, as most relevant chemical and biological reactions take place in the presence of a solvent. Including a solvation-phase intuitively, therefore, should improve the understanding of reactions in solution.[1,2]

There are two methodologies that integrate solvation effects computationally: the continuum (CSM) and discrete-continuum (DCSM) solvation models, also dubbed implicit and explicit, respectively. The CSM solvation effect as described by Errol G, Lewars,[1] involves placing "*the solute molecule in a cavity that acts as a continuous medium which simulates the sea of solvent molecules".* This suggests that the solute is induced by a dielectric continuum medium (bulk solvent) and an algorithm calculates the interaction between the solute and solution cavity. The DCSM solvation effect involves the addition of individual solvent molecules to represent the first solvation shell which in no way captures the bulk effect of solvent, but, nonetheless includes the interactions between the first solvation shell and solute. Once a system is optimised to a stationary point (relaxed), it is most often found that the solute and solvent have a reciprocated interaction which not only influences the geometry but also the reactivity and chemical properties.

Incorporating the above two methods results in a hybrid solvation model (HSM). The hybrid method is the process of applying an explicit solvation subjected to a continuum method. Outcome; the solute is present with a few solvent molecules (typically no more than four or five) and then a continuum solvation cavity is applied. Though a hybrid model is often thought of as intrinsically reasonable since the system incorporates the best of both models, the truth is that not all systems require a hybrid solvation environment. This is evident from the literature that employing a CSM only, generally gives accurate chemical properties of the molecular system, in addition to being computationally cost-effective. Application of a DCSM is often only applied in systems where solvate molecules participate in the reaction. The use of explicit molecules is computationally intensive and requires a sufficient Boltzmann average of conformers, due to the various positions the solvent can occupy with respect to the solute. The benefits of a hybrid solvation model are the accuracy of results when determining thermodynamic properties such as free energies required for pK_a values and reaction parameters.[2,3,4,6,12–14]

2.6.2. Dispersion effects

Dispersion is the weakest of the non-covalent interactions and is also referred to as London dispersion interactions (one of the attractive van der Waal-type interactions). Dispersion is related to correlation (mixed spin energies) as it is defined as the temporary attractive interaction, that is experienced (induced) when there are instantaneous dipole moments within the electron distribution between two atoms or molecules.

Dispersions involvement for computational modelling depends entirely on whether the current level of theory implemented accounts for all non-covalent interactions of the system. If not, dispersion included in the modelling can only better represent the chemical system, which influences the accuracy of theoretical thermodynamics (reaction). For *ab initio* methods; the Hartree-Fock method lacks electron correlation whereas MP2 includes electron correlation, which handles dispersion reasonably well, but generally over estimates. Though MP2 gives reasonable results, a publication by Johnson *et al*,[15] has illustrated that MP2 methods which integrate correlation effects, can undesirably predict large errors in the binding energies for many-electron systems.

If we consider DFT which is commonly used and has had great success in the field of physical organic chemistry,[2-5] we still find some drawbacks. The one issue is the inability of DFT to accurately account for dispersion interactions over a range of distances between interacting atoms or molecules: Standard DFT methods cannot accurately model dispersion interactions as they predict repulsive interactions.[16] Hybrid DFT can account for dispersion reasonably well, but only for short-range electron-electron interaction distances. Therefore, the deficiencies with regards to DFT are related to the long-range electron correlation interactions between two atoms or molecules. One can improve on the results for dispersion-interactions in certain systems, but, only when a computationally more expensive “ultrafine” grid is used.

The common non-expensive approach for improving the dispersion problem is by intuitively adding an explicit empirical term between pairs of atoms. This is called the DFT-D (dispersion-corrected DFT) technique and is commonly used to correct for DFT.[17] The corrected dispersion energy between two bodies at a range of separation can be represented as follows:

$$E_{Sys-D} = E_{Sys} + E_{disp} \tag{2.28}$$

where E_{Sys} is the energy of the system using any electronic structure method with energy correlation and E_{disp} is an empirical dispersion correction given by:

$$E_{disp} = -S_6 \sum_{i=1}^{N_a-1} \sum_{j=i+1}^{N_a} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij}) \tag{2.29}$$

here Na is the number of atoms in the system, C_6^{ij} is the dispersion coefficients which are experimentally or theoretically determined for atom pair ij, S_6 is a global scaling factor, R_{ij} is the distance between the nuclei of atom pair ij and f_{dmp} is known as a damping function to avoid singularities for when R is small. For further detail on dispersion, please refer to the references pertained to this section of work.[15–17]

For this body of work, dispersion correction was added as the system involves oligomers and non-covalent interactions which involve long-range dispersion-interactions.

2.7. Thermochemical analysis

Gaussian09 has the capability to compute thermochemical data, which is adapted and equivalent to the thermodynamic terms found in the standard text. Though the calculation of thermodynamic potentials is possible, one should be aware of the approximations implemented. The most noteworthy approximation involves treating the system as an ideal gas, hence the equations assume non-interacting particles. The different thermodynamic energies produced by Gaussian09 relate to entropy, internal energy and heat capacity. The equations used to calculate each term depending on the separable contributions from translational, rotational, vibrational and electronic motions at constant volume and temperature:

$$q(V,T) = q_{trans} q_{rot} q_{vib} q_{elec} \tag{2.30}$$

Entropy is defined by the partition function $q(V,T)$;

$$S = Nk_B + Nk_B \ln\left(\frac{q(V,T)}{N}\right) + Nk_B T\left(\frac{\partial \ln q}{\partial T}\right)_V \tag{2.31}$$

N is the number of moles present in the system, k_B is better known as the Boltzmann's constant and T represents temperature. In Gaussian, molar values are given, therefore we can divide by N/N_A and substitute $N_A k_B$ with the gas constant R:

$$S = R + R\ln\left(\frac{q(V,T)}{N}\right) + RT\left(\frac{\partial \ln q}{\partial T}\right)_V \tag{2.32}$$

Then the first term we can move into the logarithm (represent as e) and this leaves us with N=1:

$$S = R\left(\ln(q_t\, q_e\, q_r\, q_v\, e) + T\left(\frac{\partial \ln q}{\partial T}\right)_V\right) \tag{2.33}$$

The internal energy U can also be obtained from the partition function, which is written as:

$$U = Nk_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V \tag{2.34}$$

The last term, heat capacity derives from the thermal energy as;

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{2.35}$$

These equations are then used to calculate the different thermodynamic components (i.e. Gibbs free energies, enthalpy, etc.) expressed by Gaussian09. [18]

2.8. Summary

Computational chemistry modelling (CCM) is a well-developed tool, utilized for studying the behaviour of chemical systems. Modelling is achieved by employing either classic or quantum mechanics. Both attain the same outcome, generating a potential energy surface (PES) which is a mathematical relationship between the energy and geometry of the molecular system.

Molecular mechanical (MM) theory is a model based on the laws of classical physics. Each MM method employs a force field, which is a set of energy functions and parameters to calculate the PES of the molecular system. It is computationally inexpensive and commonly implemented for modelling large systems. The method does not account for electronic interactions; therefore, MM is limited and can only achieve good results for the systems for which it was parametrised. MM is often used to provide reasonable starting geometries for quantum mechanical calculations.

Quantum mechanical (QM) calculations define the system based on the electronic interactions in contrast to MM. QM theory involves solving the time-independent Schrödinger equation, where the various electronic structure methods thereof are characterised by the mathematical approximations implemented to derive the equation. There are three broad classes of electronic structure methods; semi-empirical (not discussed), *ab initio* and density functional theory (DFT) methods.

Ab initio calculations generally produce excellent quantitative results, due to the implemented non-empirical approach for the modelling. The use of no experimental parameters means that solving the Schrödinger equation is purely theory based. Typical calculations require sufficient computational resources. Hartree-Fock (HF) the simplest of the *ab initio* methods generates a reasonable molecular wavefunction, which sequentially results in reasonable answers for most calculations. The downside to HF is that the method does not treat electron correlation properly and as such, post-HF methods are the preferred *ab initio* method as they have improved electron correlation capabilities. The Møller-Plesset Pertubation Theory (MPn) method is one of the ways that is least expensive for improving on HF.

Density Functional Theory (DFT), unlike ab initio methods, is based on the Hobenberg-Kohn theorems; the ground-state properties of any system are derived from the functional of the electron density and that the functional thereof can only give the lowest energy if the input density is the true ground state density. The method has become very popular as it includes electron correlation effects and achieves qualitative results which are comparable to post-SCF *ab initio* methods at essentially HF cost.

To accurately model a molecular system, one should consider the conditions (environment) that the system resides in. One important aspect is how one treats solvation effects, as most relevant chemical and biological reactions are present in a solvent. The advances in CCM, have managed to incorporate solvation effects by either applying a continuum (CSM) or discrete-continuum (DCSM) solvation model. Another aspect to consider for a molecular system is considering the temperature at which thermodynamic analysis is performed experimentally. This is easily handled in CCM by specifying the temperature of the system. Lastly, it has been emphasized that certain methods do not account for all non-covalent interactions. Therefore, electron structure methods such as DFT are then subjected to a dispersion correction (DFT_D) that accounts for the missing electron-electron interactions. This correction only applies to systems which contain long-range dispersion interactions (e.g. dimers). In the works to follow, all aspects spoken in this chapter were employed to produce a computational model that resembles the true molecular system. This, in theory, should improve the accuracy of the reported results.

For the large molecular systems computed herein, the DFT method is ideal and shall, therefore, be implemented along with an appropriate empirical dispersion correction method. Although aware of the shortcomings of DFT, future studies will require QTAIM, IQA and FAMSEC analysis, where the AIMAll software package has recently been upgraded for explicit implementation of B3LYP wavefunctions (B3LYP-compatible IQA partitioning).[19-22]

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Chapter 3

Theoretical Investigation into the Structure of n-Butyllithium in Tetrahydrofuran.

3.1. Abstract

A conformational search protocol was implemented using DFT and Grimme's empirical dispersion in order to obtain the LECs for the diverse species of *n*-BuLi in THF solvent at –78°C. The species investigated, included the *n*-BuLi monomer, dimer and tetramer oligomers, while implementing either a continuum or hybrid solvation model. From the study, it was observed that *n*-BuLi exists in solution only as an aggregate and coordinates with up to four explicit THF solvent molecules. Of the two possible aggregate states, the tetra-solvated tetramer is found to be the more stable oligomer. Furthermore, the notion that the tetra-solvated dimer is the primary reactive species, instigated an investigation into the lability and dissociation capabilities of coordinated THF. The computational modelling shows that of the bonded four THF molecules, at least two THF molecules have the capability of dissociating, therefore, yielding a highly reactive di-solvated dimer with which to undergo a chemical reaction.

The use of STQN was implemented to obtain a possible TS for the interconversion of the unsolvated tetramer to the dimer. Although a TS was found, the stationary point was found to be inadequate. Therefore, it has been suggested that finding a valid TS requires a thorough investigation using the solvated tetramer.

3.2. Introduction

Organolithium reagents play an important role in chemistry due to their inherent reactivity with almost any functional group, which in turn has led to organolithium reagents becoming commercially cheap and accessible. Though readily available, the stereochemical characterisation of organolithium reagents in solution and in the solid state is known to have been an arduous journey.[1–3]

X-ray crystallography solid state structures of organolithium compounds have been reported, and from these findings, it was presumed that in solution, organolithium reagents are analogous in structure. Therefore, organolithium reagents should exist as aggregates in solution, and in some cases, a mixed co-existing aggregation is present due to the solvent effects. This simple hypothesis advanced the field of study to further investigate the stereochemistry of organolithium reagents in solution. Characterisation of organolithium solution state structures is possible by implementing spectroscopic techniques. The most common being one-dimensional (1-D) and two-dimensional (2-D) NMR.[1–12]

To date, the most commonly used organolithium reagent is *n*-BuLi, which has also been the subject of numerous characterisation studies.[2-8] When commercially obtained, *n*-BuLi is dissolved in a non-polar solvent. The literature states that in such a solvent, *n*-BuLi exists as a hexamer–tetramer homo-aggregate. Though it dissociates to a tetramer–dimer mixed–aggregate when a coordinating polar aprotic solvent is added to the system. THF is one such solvent that suppresses the aggregation and in doing so improves the reactivity of the reagent. This is apparent whereby pure *n*-BuLi exists as a hexamer $[n\text{-BuLi}]_6$ in the solid state, but forms a tetramer crystal structure $[n\text{-BuLi}\bullet\text{THF}]_4$ in the presence of THF.[12] Experimental kinetic studies have reported the free energy activation for *n*-BuLi interconversion between tetramer and dimer, which is approximately $\Delta G^{\ddagger} = 10.3\ \text{kcal.mol}^{-1}$ at –86 °C.[2,6]

Theoretical studies investigating the degree of aggregation and the effect from solvents for organolithium reagents are known for methyllithium, ethyllithium, sec- and tert-butyllithium.[10,11] From each study, [10,11] it was concluded that the overall trends in computed equilibrium geometries and standard free energies are in agreement with experimental works. In addition, it was noted that the charge on each lithium is independent of the size of the oligomer/ligand attached. Furthermore, the number of coordinated solvent molecules bonded to each lithium is temperature dependant. The computational studies[10,11] were carried out in either a gas phase or with microsolvation, which is instinctively not an exact representation of the real system. Therefore, the interest of this chapter focuses on implementing a hybrid solvation model (HSM) joined with a higher level of quantum theory. This should improve the accuracy when modelling the spatial structure of *n*-BuLi in THF solvent.

3.3. Computational Details

3.3.1. Solvation Model

In chapter 2 it was emphasised that an appropriate solvation model is required to accurately model chemical reactions. For the *n*-BuLi molecular system, it is known from the solid state structures that THF solvent forms strong interactions with the lithium atom.[12] Therefore, the solvation model implemented is adapted from the published works by my colleagues, whereby an amalgamation of solvation models was needed to accurately predict protonation constants (K_H) for polyamines in water.[13]

The hybrid solvation model (HSM) introduced in this work involves placing explicit solvent (THF) molecules around the solute (*n*-BuLi) to simulate the first solvation shell. The resulting molecular output, comprised of the solute and the explicit solvent, is then immersed in the continuous medium (cavity-dielectric field) to best represent the bulk solvent effects. Unfortunately, there is no guide as to the number of explicit solvents required to accurately represent the solvation shell. Therefore, it was decided to use a 0, 1, 2 and 3 mole ratios of explicit THF molecules to 1 mole of *n*-BuLi. Modelling with zero explicit molecules is equivalent to using a standard continuum-solvation model (CSM).

3.3.2. Thermodynamic Analysis

It is known that Gaussian09 can compute thermochemical data,[15] and as such, it is possible to calculate equilibrium and thermodynamic parameters relating to *n*-BuLi in THF. The first important term is enthalpy (H), which expresses the transfer of energy to and from the system based on a difference in temperature. It is expressed as:

$$H = U + RT \tag{3.1}$$

here H is the sum of the internal energy (U) and the product of the gas constant (R) at a known system temperature (T). Fortunately, in Gaussian, the result of a frequency calculation provides H with thermal correction (RT) included, which corresponds to the correction at 0 *Kelvin*. The corrected enthalpy for reactants and products can then be utilised to calculate the heats of formation (reaction enthalpy) which is calculated as follows:

$$\Delta H_{\mathrm{rxn}} = \sum H_f^{\mathrm{Produtcs}} - \sum H_f^{\mathrm{Reactants}} \tag{3.2}$$

The next thermodynamic term is the Gibbs free energy. This is defined as the work obtainable from a system at a constant temperature and volume. The Gibbs free energy term is related to entropy (*S*) and the change in *H* and is expressed as:

$$\Delta G = \Delta H - T\Delta S \tag{3.3}$$

Obtaining free energies for the system leads to calculating the free energies of reaction (ΔG_{rxn});

$$\Delta G_{\mathrm{rxn}} = \sum G_f^{\mathrm{Produtcs}} - \sum G_f^{\mathrm{Reactants}} \tag{3.4}$$

from which the equilibrium constants (K_{eq}) can be calculated:

$$\Delta G_{rxn} = -RT \ln K_{eq}$$

$$K_{eq} = \exp\left(\frac{-\Delta G_{rxn}}{RT}\right) \tag{3.5}$$

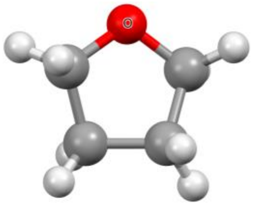
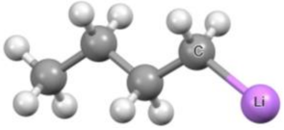
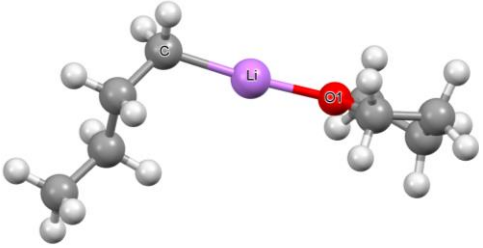
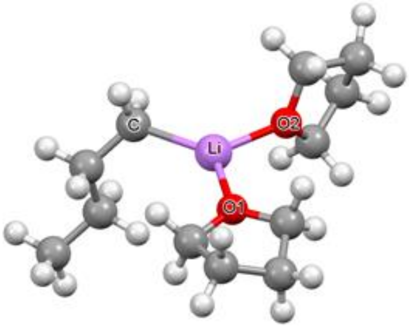
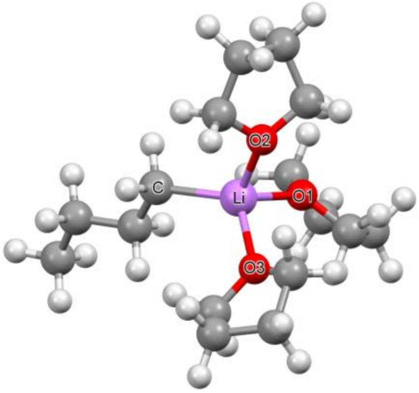
The common experimental conditions for a reaction with *n*-BuLi in THF is to chill the solution to low temperatures such as –78 °C. The low temperature environment restricts *n*-BuLi from reacting with THF, which results in deprotonation of a α-hydrogen. Hence, THF undergoes reverse cycloaddition to give an enolate of ethylene and an acetaldehyde. Therefore, all thermodynamic energy terms presented will be reported for T = –78 °C, unless stated otherwise.

3.3.3. Conformational Search Protocol

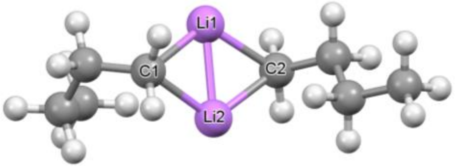
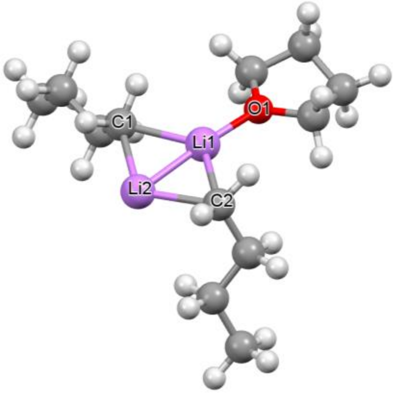
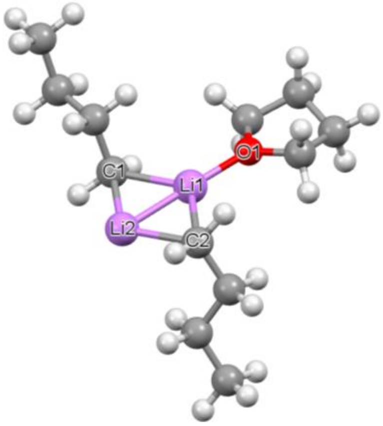
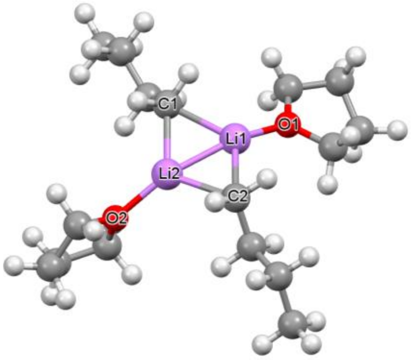
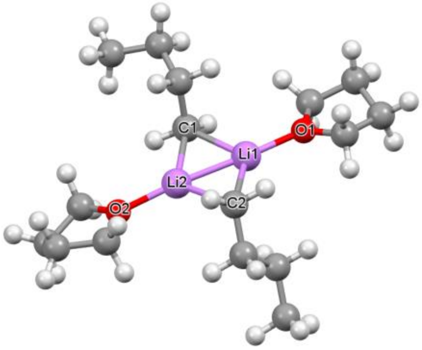
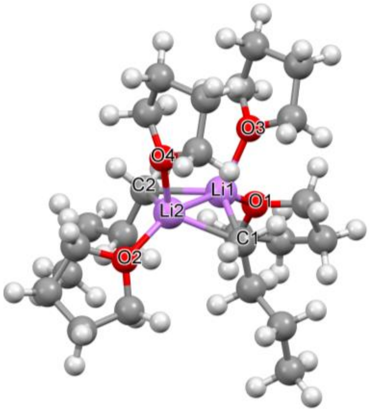
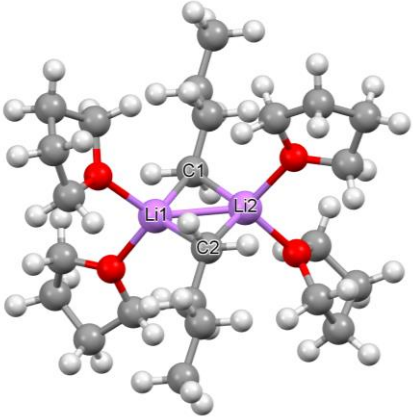
Conformational search on the various solvated species of *n*-BuLi was performed in Spartan,[15] where molecular mechanics together with the molecular mechanics force field (MMFF) and Monte Carlo algorithm were implemented. The conformational search was done by varying the torsion angles for each rotatable bond in steps of 60°. If possible, a maximum of ten unique lowest energy conformers (LECs) was retained. For now, the tetrameric form of *n*-BuLi was omitted from conformational search because literature reports the homodimer to be the reactive species.[2] Following the conformation search, the MM-discovered solvated species of *n*-BuLi were then energy optimised using Gaussian 09 Revision D01.[14] A hybrid functional of DFT at the RB3LYP/6-311++G(d,p) level of theory was employed in conjunction with the default settings for the polarisable continuum solvation model (PCM) while using THF as solvent (ε =7.4257). The conformers having an electronic energy within 2 kcal mol^{-1}, relative to the lowest in electronic energy conformer, were then subjected to frequency calculations. The vibrational frequencies were calculated at the same level of theory in order to obtain Gibbs free energies and confirm that the minimum energy structures were true stationary points on the potential energy surface (PES). The lowest energy conformer (LEC) (relative to *G*) obtained for each possible reactive species of *n*-BuLi in THF is included in Table 3.1. Furthermore, computational modelling data related to each LEC and the conformational search can be found in the Supporting Information, Appendix A.

Table 3.1. The LECs pertaining to the solvent molecule and solvated monomer (Part A) and dimer (Part B) species of *n*-BuLi in THF.

Part A.

Solvent			
THF			
Monomer *n*-Butyllithium Species			
n-BuLi		*n*-BuLi·THF	
n-BuLi·2THF		*n*-BuLi·3THF	

Part B.

Dimer *n*-Butyllithium Species			
(*n*-BuLi)$_2$			
Boat Conformation		**Chair Conformation**	
(*n*-BuLi)$_2$·THF		(*n*-BuLi)$_2$·THF	
(*n*-BuLi)$_2$·2THF		(*n*-BuLi)$_2$·2THF	
(*n*-BuLi)$_2$·4THF		(*n*-BuLi)$_2$·4THF	

*Structures were optimised at the RB3LYP/6-311++G(d,p) level of theory in Gaussian09_D01.[14]

3.4. Results and Discussion

3.4.1. Dispersion Corrected Geometries

Historically, to address long-range dispersion interactions, prohibitively expensive *ab initio* methods, such as Møller-Plesset Perturbation (MPn) theory that satisfactorily describes dispersion-interactions, have been used. Recently, advances in the field of modelling dispersion have come up with a viable and cost-effective solution to the problem, this being the empirical dispersion correction method applied to DFT methods (termed DFT-D).[16a,b] It is the most widely used and successful method for representing a chemical systems' weak interactions 'accurately' with DFT. In addition, DFT-D should also influence the accuracy pertaining to theoretical thermodynamics.[17,18] Hence, the employment of dispersion (as parameterised in Gaussian09) on the *n*-BuLi chemical systems herein. Several dispersions correction options are available in Gaussian09. As such, an appropriate empirical dispersion correction is required for obtaining a stereochemical *n*-BuLi structure that is comparable to *ab initio* MP2.

Following the selection of the LEC found in Table 3.1, certain *n*-BuLi structures were optimised with MP2 and all LECs were optimsed with Grimme's empirical dispersion correction model, GD3.[16b] Upon inspection of the MP2 optimised structures, it is observed that the geometries of solvated *n*-BuLi exhibit dispersion intramolecular interactions. The intramolecular interactions are present between the solvent [α-CH_2] groups and the butyl [CH_2] groups. Thus for the solvated dimer, the adjacent explicit THF molecules also exhibit a boat conformation. In addition, the MP2 structures feature dispersion interaction between both [β-CH_2] groups of the butyl chain, see Figure 3.1. The [CH_2- - -CH_2] dispersion intermolecular interactions were not observed for each LEC optimised with the standard RB3LYP, refer to Figure 3.1.

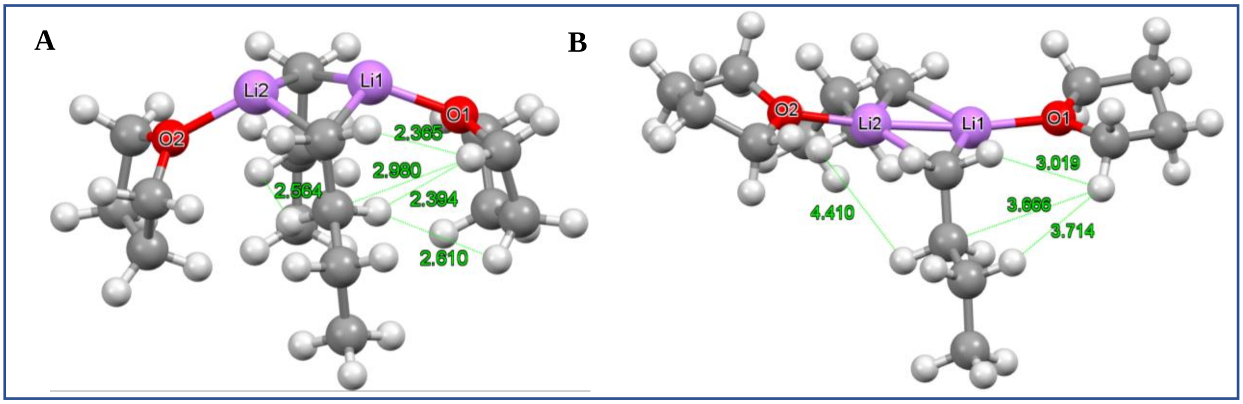
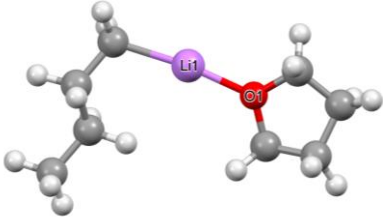
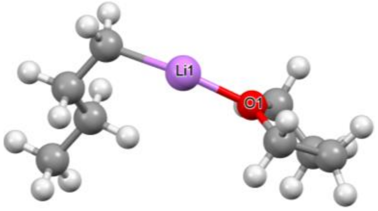
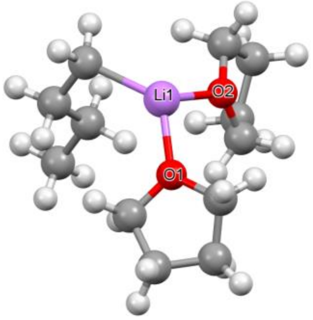
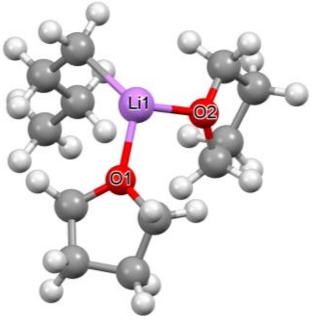
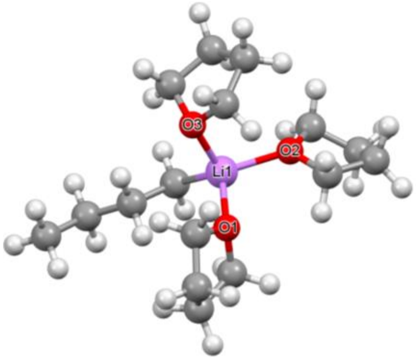
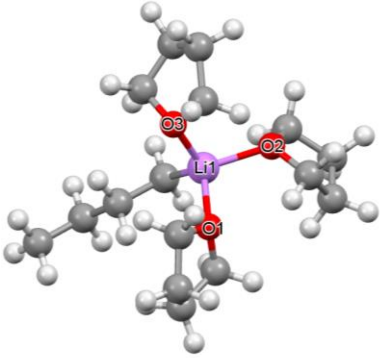


Figure 3.1. Boat conformations [(*n*-BuLi)$_2$·2THF] optimised at the RMP2/6-311++G(d,p), (**A**), and RB3LYP/6-311++G(d,p), (**B**), level of theory.

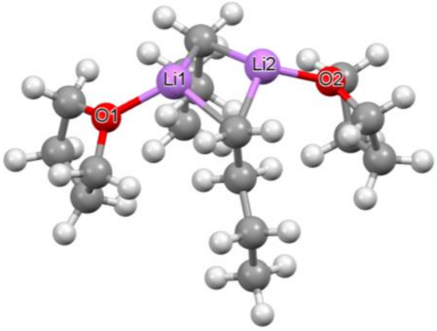
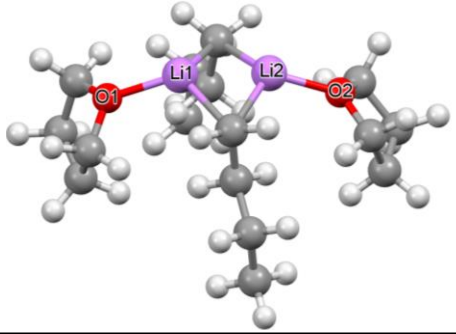
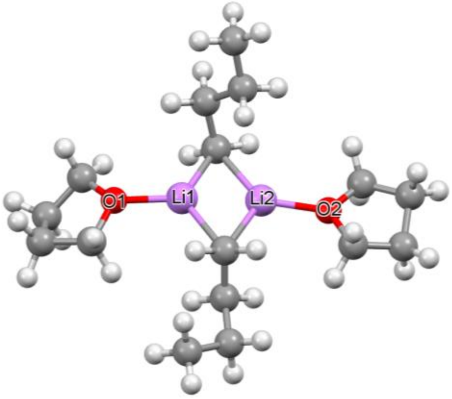
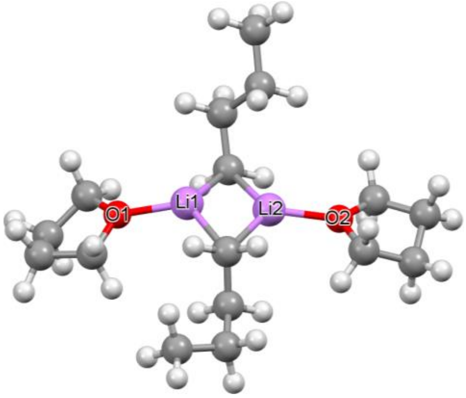
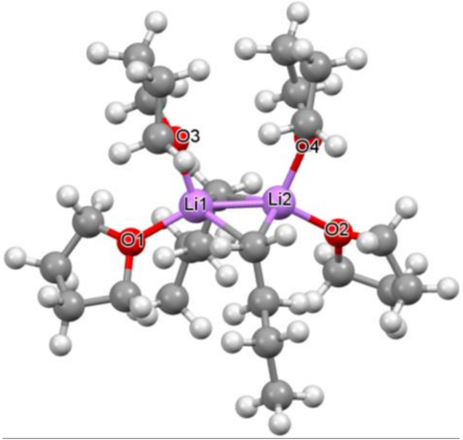
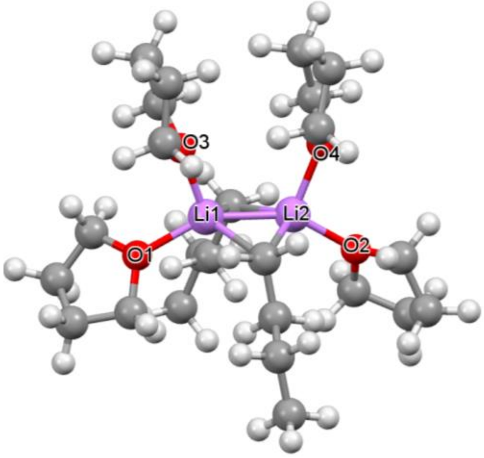
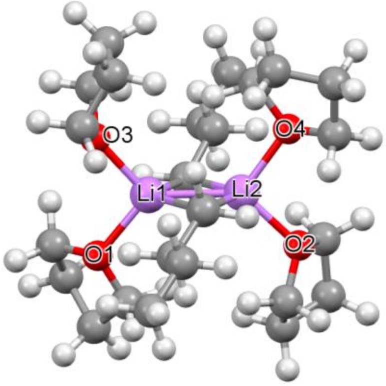
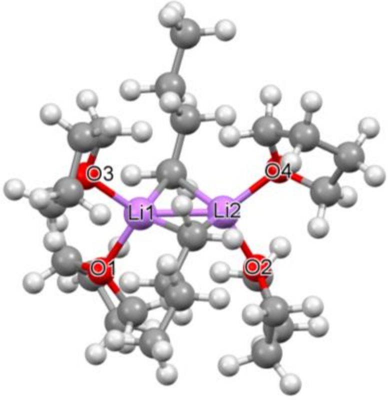
The *n*-BuLi molecular systems investigated in this work have ubiquitous dispersion-interactions. Although this is not observed with standard RB3LYP, the dispersion corrected solvated structures optimised with the RB3LYP-GD3 functional do resemble MP2, see Tables 3.2. From the MP2 and RB3LYP-GD3 optimised monomer and dimer *n*-BuLi geometries, it is observed that as the number of coordinated THF to lithium increases, further dispersion-interactions are observed between each solvent molecule and between the solvent and butyl groups. Furthermore, the extent to which each molecules stereochemistry is influenced by solvent interactions imposed by empirical dispersion, concludes that the LECs optimised with RB3LYP-GD3 are to be utilised throughout the rest of the study. The LEC structures should be adequate for computing frequency calculations to establish which solvated species is most favourable in terms of the electronic and thermodynamic energies.

Table 3.2. The dispersion-corrected solvated LECs of monomers (Part A) and dimers (Part B) of *n*-BuLi species optimised at the RMP2 and RB3LYP-GD3 levels of theory.

Part A.

Monomer *n*-Butyllithium Species		
	MP2	**B3LYP–GD3**
[*n*-BuLi·THF]		
[*n*-BuLi·2THF]		
[*n*-BuLi·3THF]		

Part B.

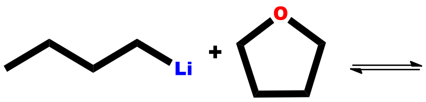
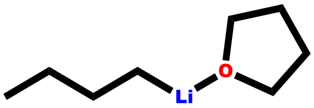
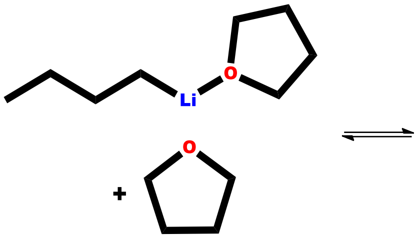
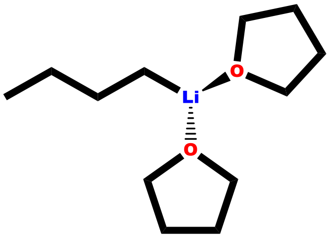
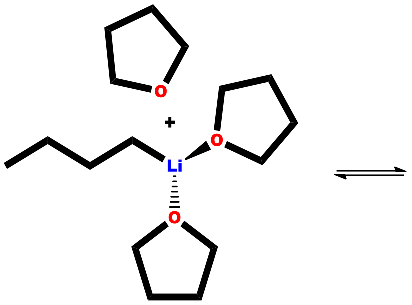
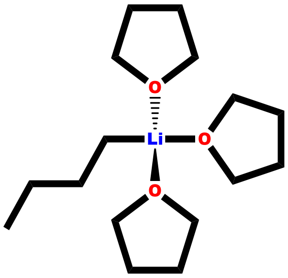
Dimer *n*-Butyllithium Species		
	MP2	**B3LYP–GD3**
Boat: [(n-BuLi)$_2$·2THF]		
Chair: [(n-BuLi)$_2$·2THF]		
Boat: [(n-BuLi)$_2$·4THF]		
Chair: [(n-BuLi)$_2$·4THF]		

3.4.2. Identifying the Favourable Solvated Structure

The next step involves identifying which solvated species of *n*-BuLi is most favourable. Selecting the most stable species requires thermodynamic data. Hence, all *n*-BuLi compounds shown in Table 3.2 were subjected to frequency calculations (at the same DFT-D level of theory) that were needed to compute the solvation reaction formation energies.

Table 3.3 reports the formation energies for each solvated state of the *n*-BuLi monomer. Each stepwise addition of THF stabilises the system, where the change in electronic energy (ΔE_{rxn}) is c.a. –10 kcal.mol^{-1}. When considering the reaction free energies, the addition of the first THF molecule is favoured with ΔG_{rxn} equal to –2.15 kcal.mol^{-1}. Addition of the second and third THF solvent molecule also have favourable stability, where ΔG_{rxn} is equal to –1.80 and –2.93 kcal.mol^{-1}, respectively. Although each system in Table 3.3 is favourable upon increasing the number of coordinated THF, the amount by which ΔG_{rxn} stabilises the system is c.a. –2 kcal mol^{-1}.

Table 3.3. Solvation reaction energies for the formation of THF-solvated monomeric species of *n*-BuLi at the RB3LYP–GD3/6-311++G(d,p) level of theory.

Reactants	**Products**	ΔE_{rxn}	ΔG_{rxn}	ΔH_{rxn}
		kcal.mol^{-1} (Products-Reactants)		
 [*n*-BuLi] + [THF]	 [*n*-BuLi·THF]	–9.51	–2.15	–8.12
 [*n*-BuLi·THF] + [THF]	 [*n*-BuLi·2THF]	–11.45	–1.80	–10.01
 [*n*-BuLi·2THF] + [THF]	 [*n*-BuLi·3THF]	–8.97	–2.93	–8.11

The computationally modelled formation of the non-solvated dimer of *n*-BuLi (Reaction 3.6) generated $\boldsymbol{\Delta}E_{\mathrm{rxn}}$, $\boldsymbol{\Delta}G_{\mathrm{rxn}}$ and $\boldsymbol{\Delta}H_{\mathrm{rxn}}$ of –15.7, –7.5 and –13.9 kcal mol^{-1}, respectively. Clearly, the formation of the *n*-BuLi dimer is significantly favourable over the solvated monomer.

$$(n\text{-BuLi}) + (n\text{-BuLi}) \rightleftarrows (n\text{-BuLi})_2 \qquad \Delta G = -7.5\ \text{kcal.mol}^{-1} \qquad (3.6)$$

In addition, the value of ΔG_{rxn} for generating a dimer is far more favourable than the combination of all the reaction free energies related to the addition of three THF molecules coordinated to the *n*-BuLi monomer. This result is a perfect agreement with the literature,[5–7] which reports that *n*-BuLi exists as an oligomer in the polar aprotic THF solvent and not as a monomer.

When coordinating THF solvent to the *n*-BuLi dimer, it is observed that the addition of explicit THF molecules also increases the stability of the dimeric system, see Table 3.4.

$$\text{Boat:}\quad (\text{n-BuLi})_2 + 2\text{THF} \rightleftarrows (n\text{-BuLi})_2{\cdot}2\text{THF} \qquad \Delta G = -8.49\ \text{kcal.mol}^{-1} \qquad (3.7)$$

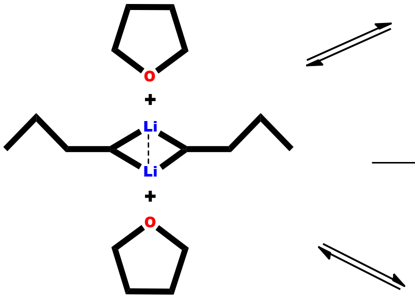
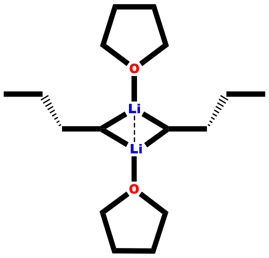
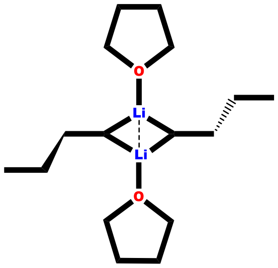
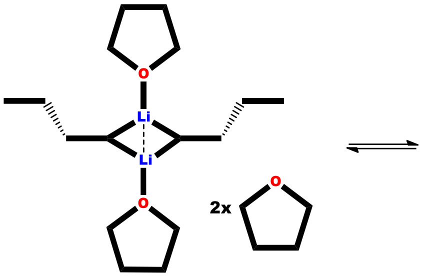
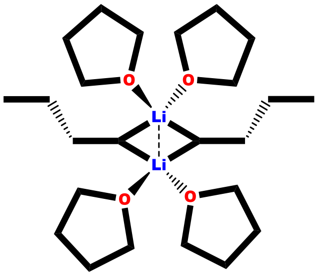
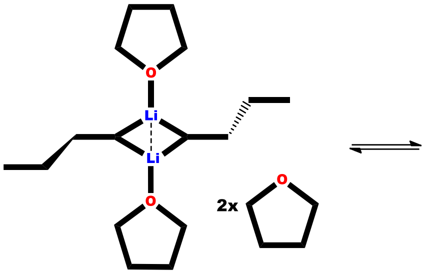
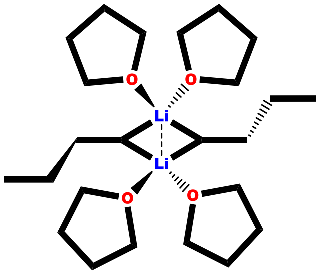
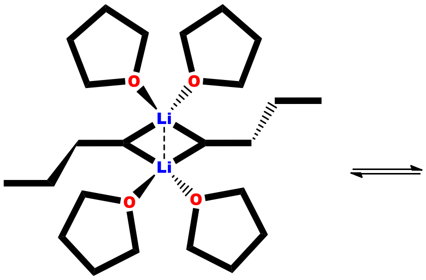
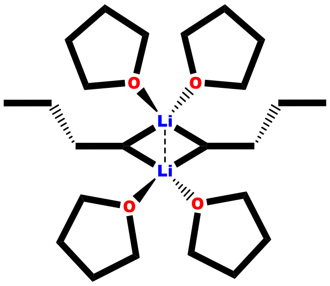
$$(n\text{-BuLi})_2{\cdot}2\text{THF} + 2\text{THF} \rightleftarrows (n\text{-BuLi})_2{\cdot}4\text{THF} \qquad \Delta G = -2.37\ \text{kcal.mol}^{-1} \qquad (3.8)$$

$$\text{Chair:}\quad (\text{n-BuLi})_2 + 2\text{THF} \rightleftarrows (n\text{-BuLi})_2{\cdot}2\text{THF} \qquad \Delta G = -8.07\ \text{kcal.mol}^{-1} \qquad (3.9)$$

$$(n\text{-BuLi})_2{\cdot}2\text{THF} + 2\text{THF} \rightleftarrows (n\text{-BuLi})_2{\cdot}4\text{THF} \qquad \Delta G = -2.75\ \text{kcal.mol}^{-1} \qquad (3.10)$$

Unlike in the case of the monomer, the reaction free energy for coordination of the first THF to each *n*-BuLi is larger and more stabilising than the addition of consecutive THF molecules. From the computed thermodynamic data, it is possible to conclude that not only does *n*-BuLi exist as a dimer in solution, but each *n*-BuLi can coordinate at least two THF molecules. Equations 3.7 and 3.9 conclude that the boat conformation coordinated with two THF molecules is found to have the lowest free energies and is, therefore the more stable di-solvated conformation. When looking at equations 3.8, 3.10 and the reaction energies found in Table 3.4, it is observed that the [$(n$-BuLi$)_2{\cdot}4$THF] solvated species of *n*-BuLi is predicted to be the most favourable dimeric structure, thus far. Furthermore, For the tetra-solvated species, it is observed that overall the reaction energies between the chair and boat conformations are equivalent (differ by less than 1 kcal mol^{-1}). Hence, each conformation is found in solution and based on the energies alone, deciding the most stable conformation is arguable.

Table 3.4 Solvation reaction energies for the formation of THF-solvated dimeric species of *n*-BuLi at the RB3LYP–GD3/6-311++G(d,p) level of theory.

Reactants	**Products**	ΔE_{rxn}	ΔG_{rxn}	ΔH_{rxn}
		kcal.mol^{-1} (Products-Reactants)		
 [*n*-BuLi]$_2$ + 2[THF]	 Boat: [(*n*-BuLi)$_2$·2THF]	–27.11	–8.49	–23.78
	 Chair: [(*n*-BuLi)$_2$·2THF]	–24.19	–8.07	–21.43
 Boat: [(*n*-BuLi)$_2$·2THF] + 2[THF]	 Boat: [(*n*-BuLi)$_2$·4THF]	–20.35	–2.37	–18.13
 Chair: [(*n*-BuLi)$_2$·2THF] + 2[THF]	 Chair: [(*n*-BuLi)$_2$·4THF]	–23.85	–2.75	–20.89
 Chair: [(*n*-BuLi)$_2$·4THF]	 Boat: [(*n*-BuLi)$_2$·4THF]	0.59	–0.05	0.41

3.4.3. Investigating the Solvent Effects.

We know *n*-BuLi exists as an oligomer due to the solvent effects of THF, but what is the optimum ratio of solvent to *n*-BuLi? The tetra solvated species is found to be the favourable solution state as the dimeric form of *n*-BuLi favours a 2:1 ratio over the 1:1 ratio of THF to *n*-BuLi, but only by –2.37 and –2.75 kcal.mol^{-1} for the boat and chair conformations, respectively. Furthermore, the boat conformation is marginally lower in energy by 0.05 kcal.mol^{-1} compared to the chair conformation, suggesting that with such a small difference in energies, both species ought to be present in solution. From Tables 3.3, it was observed that the monomeric *n*-BuLi species favours a ratio of three THF to one *n*-BuLi, so does the same hold for the dimeric conformation? Therefore, two additional THF molecules were introduced to the (n-BuLi)$_2$·4THF conformational system and a geometry optimisation conducted. The output for the optimisation of the now (n-BuLi)$_2$·6THF species was unsuccessful. The reason being that the stereochemistry of (n-BuLi)$_2$·4THF is already crowded and as such the dimeric system cannot accommodate two addition solvent molecules. The optimisation energy output plot is seen in Figure 3.2, where the lowering of energy is a result of the

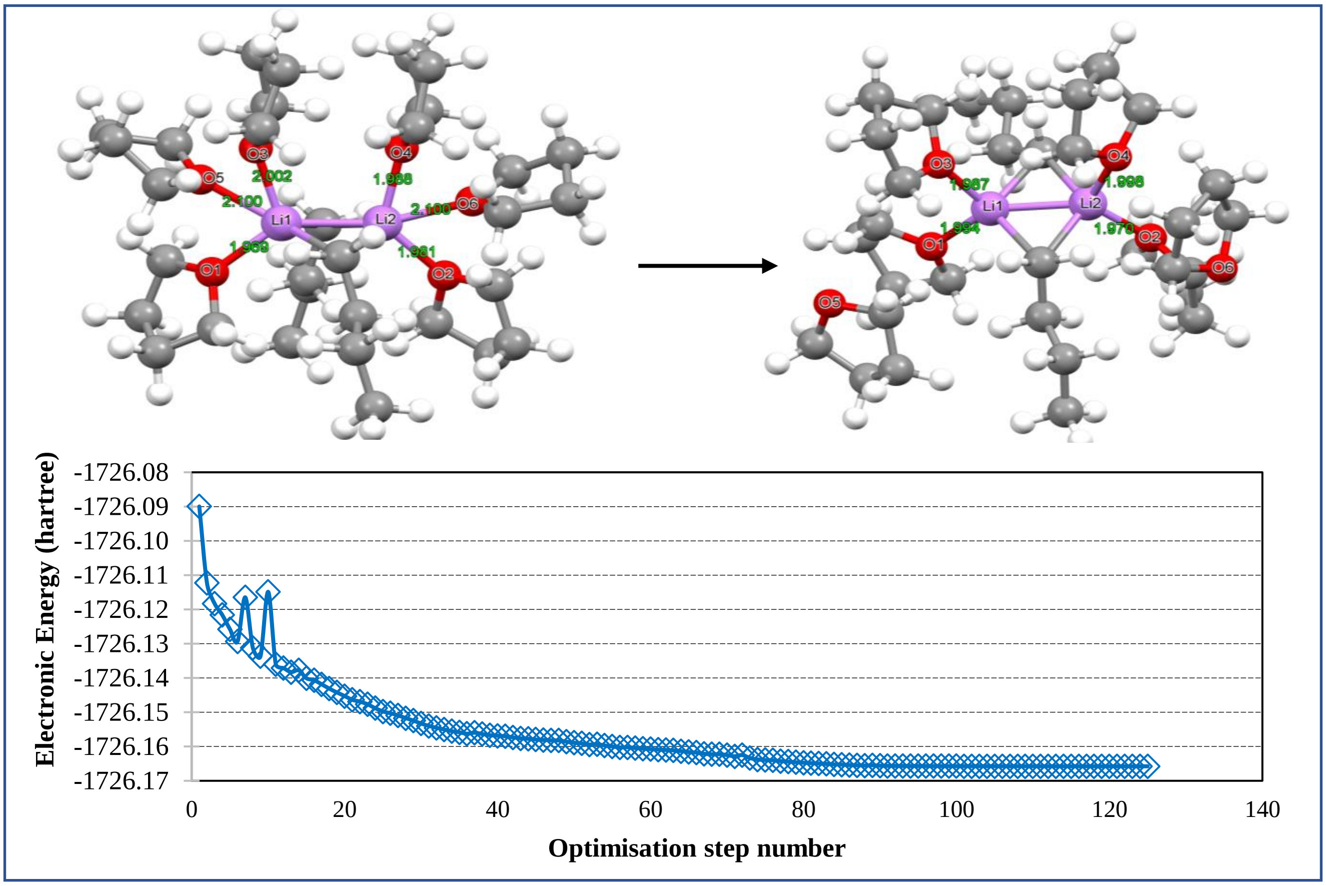


Figure 3.2 Geometry optimisation profile for the hexa-solvated dimer species of *n*-BuLi. Calculations were done at the RB3LYP-GD3/6311++G(d,p) level of theory.

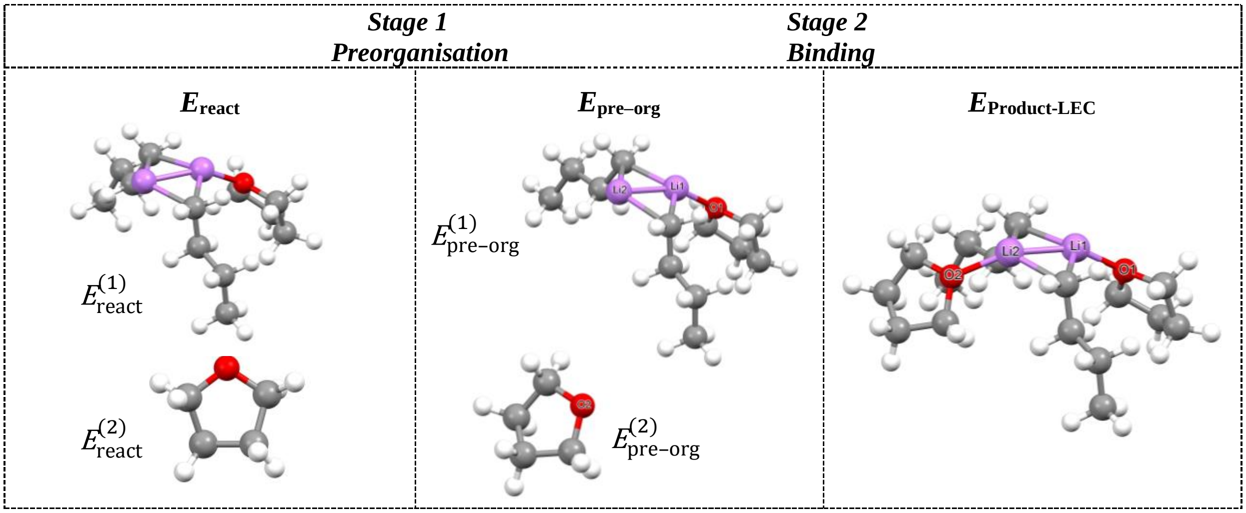
two additional solvent molecules actively leaving from the already stable (n-BuLi)$_2$·4THF molecular system. Therefore, the (n-BuLi)$_2$·4THF species is considered the optimum and favourable dimeric structure. That being stated, is (n-BuLi)$_2$·4THF the preferred reactive species when considering that two THF molecules could not be added due to steric crowding. Would it be possible to model reactions with the tetra-solvated dimer?

To gain some insight, a hypothetical scenario in solution has been considered, namely that the tetra-solvated dimer species undergoes dissociation of either one or two interacting solvent molecules. Hence, the loss of coordinating THF molecules, generating a more reactive (n-BuLi)$_2$·3THF or (n-BuLi)$_2$·2THF species, respectively. To determine if such a scenario is even possible for solvated n-BuLi systems, the binding energies between a THF solvent molecule(s) and n-BuLi have been computed.

A. Binding and Pre-Organisation Energies.

To form a favourable reactive product, the reactants must change structurally to accommodate the new environment. This change in stereochemistry can be perceived as a pre-organisation process of reactants to attain exactly the same structures observed in a final product. Therefore, the energy difference $\sum E_{\text{pre–org}} - \sum E_{\text{react}}$ can be called a pre-organization energy, an energy ‘penalty’ the structure gains in order to prepare the reactive components for binding process. Hence, binding energy can be obtained from $E_{\text{prod}} - \sum E_{\text{pre–org}}$ and finally ΔE_{rxn} can be expressed:

$$\Delta E_{\text{rxn}} \quad = \quad E_{\text{def}} + E_{\text{bind}} \quad = \quad E_{\text{prod}} - \sum E_{\text{react}} \qquad (3.11)$$



Scheme 3.1. A simplified fragment approach for partitioning the energies related to solvent interaction with n-BuLi.

The two terms in equation 3.11 are dubbed the deformation (E_{def}) and binding (E_{bind}) energies. The two energy terms are illustrated in Scheme 3.1. At stage 1, E_{def} is defined as the deformation of each reactant (E_{react}) into the individual pre-organised fragments $E_{\text{pre-org}}$;

$$E_{\text{def}} = \sum E_{\text{pre-org}} - \sum E_{\text{react}} \tag{3.12}$$

E_{def} is generally a positive value, which is indicative of the strain the molecular fragments gain in-order to position itself before bonding occurs. The second stage represents the binding between the solvent (THF) and (*n*-BuLi)·THF, which leads to the formation of the more stable product (*n*-BuLi)$_2$·2THF. The E_{bind} term is calculated as follows;

$$E_{\text{bind}} = \sum E_{\text{prod}} - \sum E_{\text{pre-org}} \tag{3.13}$$

E_{bind} places emphasis on the affinity for bond formation and is, therefore, generally, a negative value. In Table 3.5, the computed E_{def} and E_{bind} energies are reported for the stepwise addition of one to four solvent molecules. The reported values were obtained using single point electronic energy calculations in Gaussian09, where each fragment pertaining to the products was separated into the two $E_{\text{pre-org}}^{(n)}$ chemical moieties. From the data in Table 3.5 positive E_{def} values are observed, which indicates that the molecular system undergoes more strain (crowding) as the number of coordinating THF molecules increases. Furthermore, we have a binding energy of c.a. –13 kcal.mol^{-1} for the stepwise additions of explicit THF. This value indicates that the stability of the *n*-BuLi dimeric system is influenced by the strong affinity for solvent interactions.

Table 3.5. Computed E_{def} and E_{bind} energies for the stepwise addition of THF to the boat conformation of *n*-BuLi–dimer.

Reactants		**Products**	$\mathbf{E_{def}}$	$\mathbf{E_{bind}}$	$\mathbf{\Delta E_{rxn}}$
				kcal.mol^{-1}	
(*n*-BuLi)$_2$ + THF	⇄	(*n*-BuLi)$_2$·THF	0.36	–13.75	–13.39
(*n*-BuLi)$_2$·THF + THF	⇄	(*n*-BuLi)$_2$·2THF	0.68	-13.02	–12.34
(*n*-BuLi)$_2$·2THF + THF	⇄	(*n*-BuLi)$_2$·3THF	1.00	–11.05	–10.06
(*n*-BuLi)$_2$·3THF + THF	⇄	(*n*-BuLi)$_2$·4THF	2.28	–13.14	–10.85
(*n*-BuLi)$_2$·2THF + 2THF	⇄	(*n*-BuLi)$_2$·4THF	2.54	–23.45	–20.91

Although binding energies are informative about the stability imposed by solvent effects, it does not ascertain quantitatively for discerning the solvent dissociation capabilities. An analogy would be that of ionisation of an atom. A THF solvent molecule can be thought of as an electron bound to an *n*-BuLi dimer, where the favourable system hosts four THF in the ground state. The energy required to remove one solvent molecule should be far less than the removal of consecutive THF molecules. A simple scan protocol has been implemented to compute the approximate change in electronic energy related to the affinity of *n*-butyllithium dimer for THF.

B. Dissociation Energies: A PES Scan Approach.

The scan protocol involves elongating the lithium–oxygen bond until complete separation of the components, resulting in bond dissociation. Until now, all calculations involved a closed shell model (restricted) for handelling electron spin, but when modelling involves bond dissociation, implementation of an open shell model (unrestricted) for handling the electron spin is required and therefore, was applied. The difference in relative energies between the scan structures and the optimised LEC should give an indication of the bond energy affinity. In Figure 3.3, the relative electronic energies for the lithium-oxygen bond dissociation is plotted, where the Li—O bond length is expanded by 2.0 Å in 0.1 Å increments.

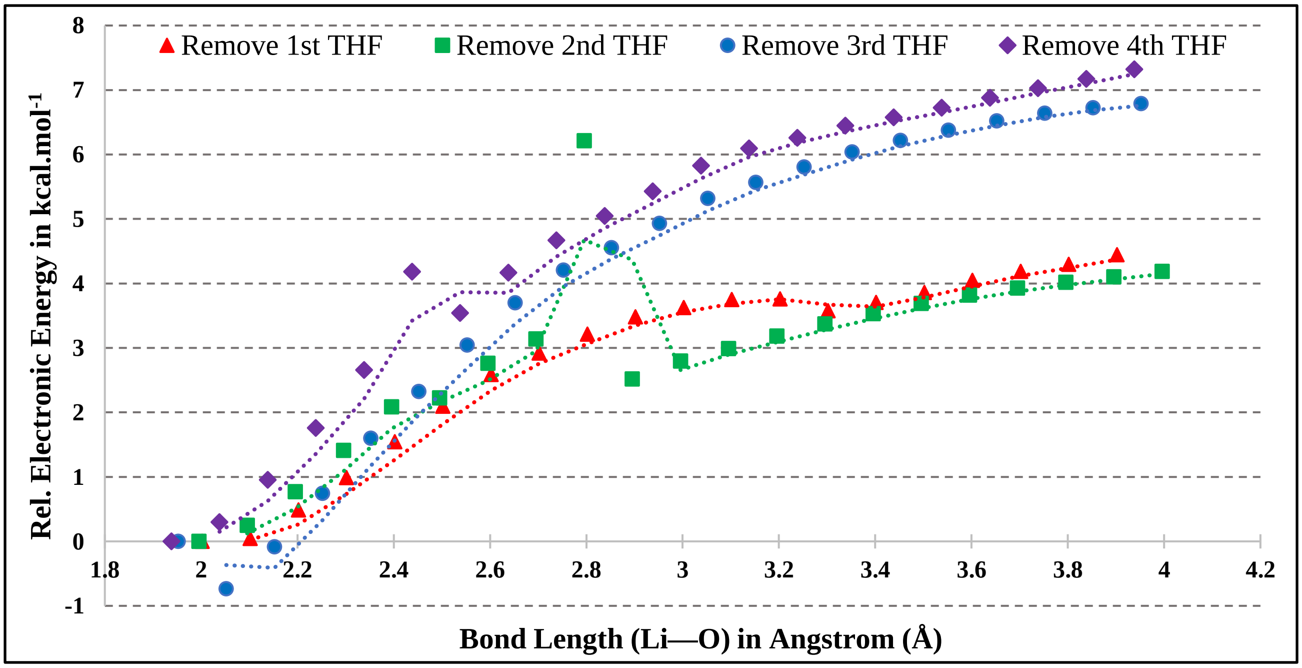


Figure 3.3. Scan plot: Stretching the individual lithium—oxygen bond lengths by 2.0 Å to evaluate the solvent interaction.

Separating the first and second THF solvent molecules increase the energy of the system by c.a. ~4.4 kcal.mol^{-1}. The energy required for separating the third and final THF molecules is equal to c.a. ~7 kcal.mol^{-1}. The difference in energies supports the notion that solvent dissociation is possible when considering the first two solvent molecules. Although possible, dissociation can only take place if enough energy is gained by the system to cleave the bonds. Since the third and fourth solvent molecules require almost twice as much energy in order to dissociate, it is unambiguous that the dimeric form will always have at least a 1:1 ratio of THF solvent interacting with *n*-BuLi. Due to the nature of the plots, one could say that the electronic energy values found in Figure 3.3 do not correlate with those in Table 3.5. Reason being that with regards to binding energies, one assumes the complete separation of each moiety. Whereas in a scan, each point along the plot is optimised with THF still present, hence influencing the stability of the system.

So far it has been reported that the *n*-BuLi dimer is the preferred species when compared to the monomer. In addition, the theoretical study has found the tetra-solvated dimer to be the favourable dimeric species as reported in the literature.[7] When considering modelling a chemical reaction involving solvated *n*-BuLi, the di-solvated species is also a viable candidate; note that the energy required to elongate the bond might decrease in the presence of the on-coming and interacting reagent (e.g. 2-bromothiophene).

3.4.4. Tetramer

Literature reports the solution state of *n*-BuLi to be a mixed aggregate,[7] with the tetramer and dimer species present simultaneously;

$$(n\text{-BuLi})_4 \quad \rightleftarrows \quad 2(n\text{-BuLi})_2 \qquad \Delta G^{\ddagger}_{(-86\ ^\circ\mathrm{C})} = {\sim}10.3\ \mathrm{kcal.mol}^{-1} \tag{3.14}$$

where $\Delta G^{\ddagger}$ is the free energy interconversion barrier published in the literature.[6] Additionally, it is also reported that the dimer is primarily the reactive species and that the ratio of dimer to tetramer increases as the temperature of the system decreases.[6] For this section, a conformational search was conducted for both the non–solvated and tetrasolvated tetramer *n*-BuLi species. The crystal structure, CSD–WAFJES,[12] served as the input for conducting the conformational protocol. The protocol involved computing at the UB3LYP/6-311++G(d,p), level of theory which included Grimme’s empirical dispersion correction model, GD3.[16b] The several computed outputs were valuable as the initial optimised structures were spontaneously metamorphosed into a structure that resembles a polyhedron composed of four triangular faces (tetrahedron), see Figure 3.4. The unique tetrahedron stereochemistry was then submitted for further optimisation until a satisfactory stationary point was found exhibiting no imaginary frequencies. From Figure 3.4 it is observed that both the (n-BuLi)$_4$ and (n-BuLi)$_4$·4THF LECs have the alpha carbons (C_α) exhibiting unique interaction with the face of the Li$_4$ tetrahedral structure.

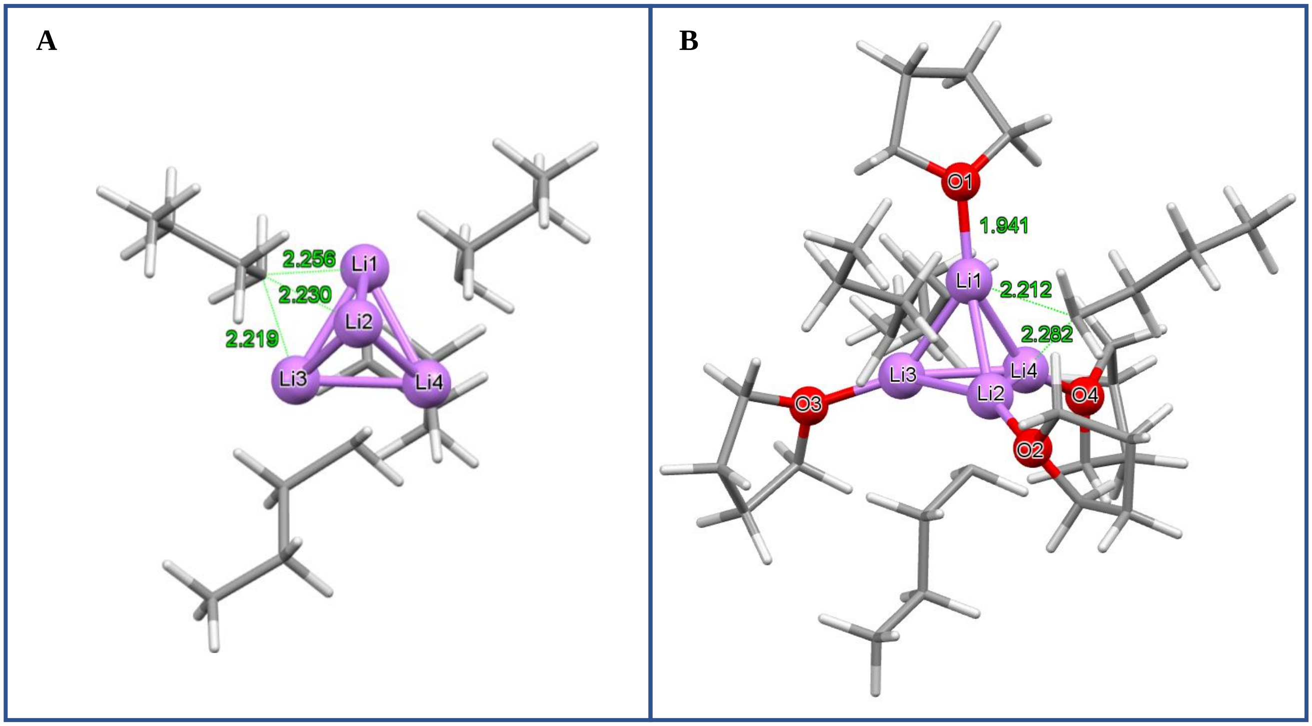


Figure 3.4. The LECs of the non-solvated (A) and solvated (B) tetrameric species of n-BuLi in THF.

Now that a ground state tetramer was obtained, it is possible to report on the thermodynamic data related to equilibrium between the tetra-solvated dimer and tetramer:

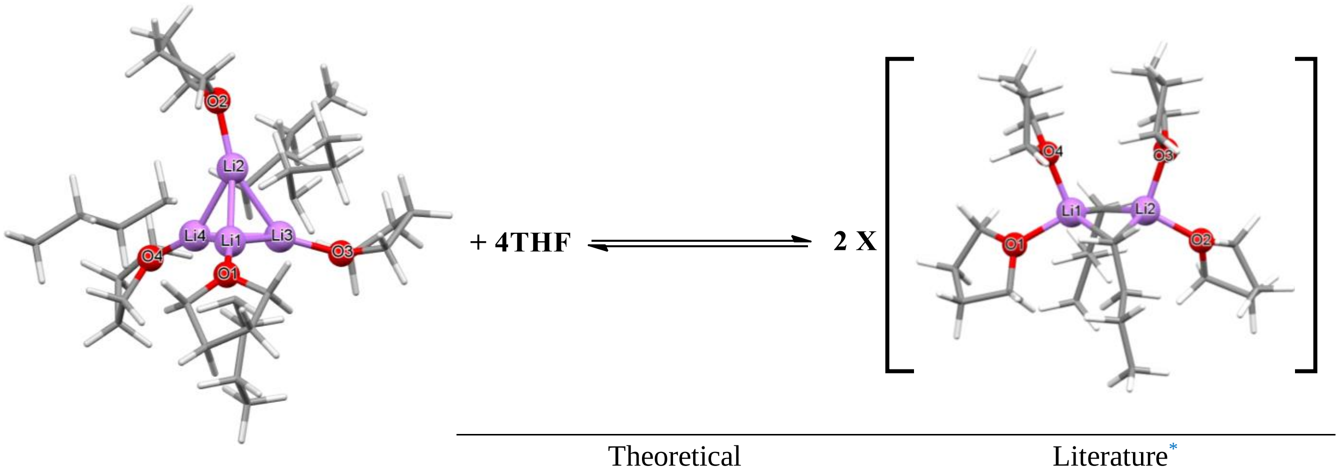
$$(n\text{-BuLi})_4\cdot 4\text{THF} + 4\text{THF} \rightleftarrows 2[(n\text{-BuLi})_2\cdot 4\text{THF}] \qquad (3.15)$$

From the thermodynamic data reported in Table 3.6, it is noticed that the results differ appreciably with that of literature. Although, both experimental and computational data agree that for the tetramer to dissociate into the dimer pair at equilibrium, the reaction is to be exothermic. The zero-point corrected electronic energies equal to c.a. –15 kcal mol^{-1}, proposes that 2(n-BuLi)$_2$·4THF is electronically the favoured n-BuLi species "structurally". So once the more stable tetramer converts to the dimer, a preferred reactive species is obtained with which to undergo post-reactions. Importantly, the computed and literature data agree qualitatively, and both indicated an exothermic reaction with rather a small positive ΔG value.

Table 3.6. Thermodynamic data (in kcal mol^{-1}) pertaining to the *n*-BuLi equilibrium species in THF (–88°C).

Structures

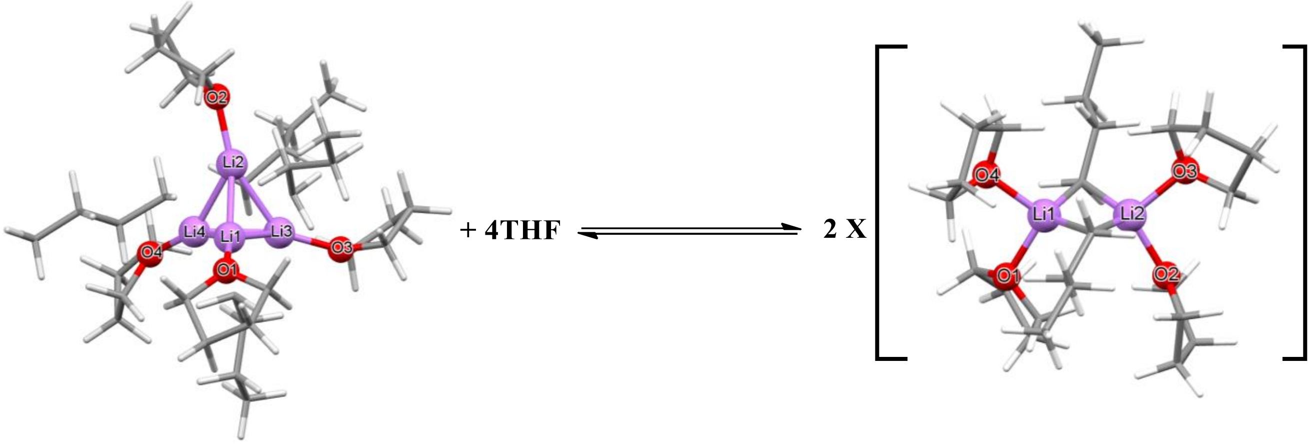
A) Boat Conformation



	Theoretical	Literature*
ΔE_{ZPVE}	-14.76	—
ΔG_{rxn}	5.20	1.42 (± 0.9)
ΔH_{rxn}	–14.54	–2.06 (± 1.1)
ΔS_{rxn}	–20.81	–18.8 x10^{-3} (± 4.4 x10^{-3})

Structures

B) Chair Conformation



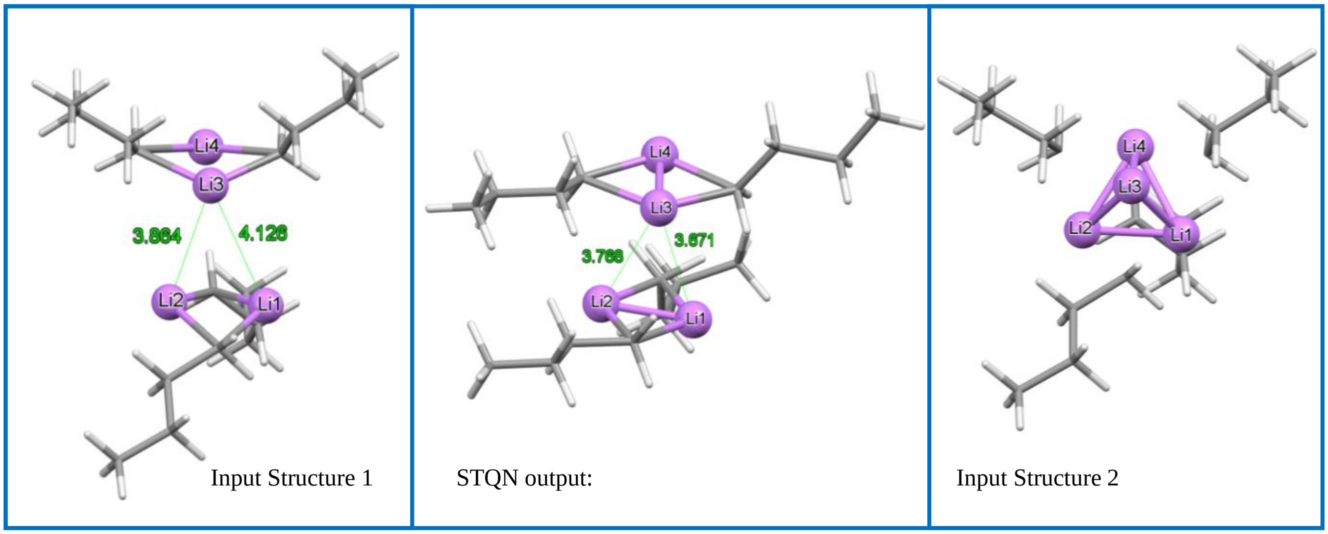
	Theoretical	Literature*
ΔE_{ZPVE}	–15.40	—
ΔG_{rxn}	5.25	1.42 (± 0.9)
ΔH_{rxn}	–15.36	–2.06 (± 1.1)
ΔS_{rxn}	–21.72	–18.8 x10^{-3} (± 4.4 x10^{-3})

[a] Experimental gibbs free energies are reported at –88°C;[6b] ΔH_{rxn} & ΔS_{rxn} are the reported standard enthalpy and entropy of formation, respectively.

Locating a Transition State

From the published free energy activation, refer to Eq. 3.14, it follows that the interconversion of the tetramer into dimer goes through a TS on the potential energy surface. Therefore, attempts were made to find a TS using the Synchronous Transit-Guided Quasi-Newton (STQN; developed by H. B. Schlegel and co-workers)[20,21] method implemented in Gaussian09. The input structures were that of *n*-BuLi using only the CSM model, see Figure 3.5. The computational modelling resulted in a stationary point having one negative imaginary frequency mode. Although a stationary point holding one imaginary frequency was found, the STQN output was not adequate for conducting an intrinsic reaction coordinate (IRC)[22] in Gaussian09.[14] Firstly an IRC calculation tries to obtain both the minima along the reaction path. If either minimum resembles the products and reactants, then the transition state is deemed acceptable. In the case of TS obtained for the unsolvated *n*-BuLi tetramer, the IRC calculations failed due to the weak negative frequency mode, making it difficult for the computation to link two minima along a reaction path.

The above failed attempt strongly suggests that one should search for the TS of solvated rather than unsolvated tetramer. Unfortunately, due to the timeframe of the study, a thorough investigation on locating a ‘proper’ TS for the formation or dissociation of the tetramer was not conducted.



Input Structure 1

STQN output:

Input Structure 2

Figure 3.5. The structures used in the STQN calculation for acquiring a TS for the *n*-BuLi tetramer to dimer interconversion.

3.5. Conclusions

The conformational search protocol was effective in determining the LECs for all possible oligomer states of *n*-BuLi in THF. Furthermore, the quality of the B3LYP-generated structural geometries was improved by implementing Grimme's empirical dispersion correction; they compare well with those computed at the MP2 level. It is observed that not only does *n*-BuLi interact and coordinate with several THF molecules, the explicit THF also influences the stereochemistry of the aggregates. Comparison of the solvation reaction energies concludes that *n*-BuLi has significant stability when the species is aggregated, therefore, the monomer does not exist in solution. In addition, the stability of the aggregate is influenced by the number of coordinated THF. Hence, the dimer can facilitate up to four coordinated THF molecules, with the tetra-solvated dimer having the greatest stability.

For the purpose of modelling a chemical reaction, the tetra-solvated dimer is not ideal due to the crowding of four explicit THF molecules. An investigation into the dissociation capabilities shows that the more stable tetra-solvated dimer can exist (at equilibrium) with the more reactive di-solvated dimer, which serves as an improved input for modelling chemical reaction mechanisms.

Lastly, comparison of the tetramer and dimer aggregates showed that the tetra-solvated tetramer is favoured in terms of Gibbs free energies (c.a. –5.2 kcal mol^{-1}). This supports the notion that the rate-determining step involving *n*-BuLi is the interconversion process from tetramer to dimer.

3.6. References

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Chapter 4

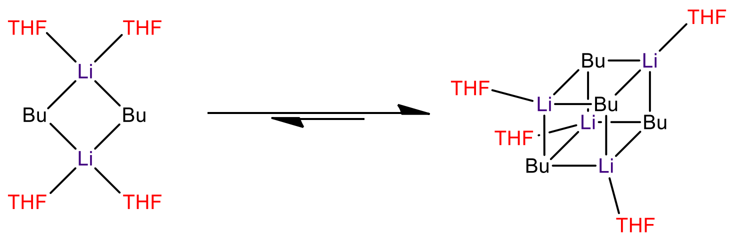
Spectroscopic & Theoretical NMR Study, into the Structure of n-Butyllithium in Tetrahydrofuran.

4.1. Abstract

n-BuLi is reported to exist as a mixed-aggregate of dimer and tetramer in THF. With the computed LECs of solvated dimer and tetramer, theoretical one-dimensional ^{1}H, ^{13}C, and ^{7}Li NMR data were generated in Gaussian09. With this data and an appropriate reference molecule, theoretical chemical shifts were calculated to produce theoretical one-dimensional NMR spectra. The spectra were utilised in the assigning of chemical shifts and for the qualitative comparison with experimental spectra. The ^{1}H and ^{7}Li NMR spectra provided a conclusive synergy between experimental and theoretical results. They confirmed the mixed-aggregation of *n*-BuLi in THF as the tetra-solvated dimer and tetramer. Furthermore, the experimental ^{1}H and ^{7}Li NMR spectra showed that the ratio of dimer to tetramer increases as the temperature of the system is lowered. Lastly, the absence of ^{13}C NMR spectra in the literature was clarified as most likely due to the ambiguity of assigning observed shifts to individual nuclei. Theoretical ^{13}C NMR study was not particularly helpful in this regard, but it was observed that the ambiguous spectra are a result of several individual nuclei having equivalent chemical shifts.

4.2. Introduction

The organolithium compound *n*-butyllithium (*n*-BuLi) has long been a widely used and studied reagent in the field of chemistry.[1] Over the years, a considerable amount of work has been done in the field of nuclear magnetic resonance (NMR) spectroscopy and x-ray crystallography on defining the stereochemical characterisation of *n*-BuLi.[2,3] It has been reported that for the solid-state structure, a tetra-solvated tetramer is observed,[3] while a mixed-aggregate (tetramer-dimer equilibrium) exists in tetrahydrofuran (THF) solution. Until now, the incomplete characterisation of the solvation state of *n*-BuLi provided the opportunity for implementing theoretical techniques to confirm the solvation-state structure. To date, theoretical computational studies have been implemented for investigating the degree of aggregation and the effect of solvent on various organolithium reagents,[4] however, no theoretical works relating to *n*-BuLi have been published so far. The diffusion-ordered NMR studies by Willard & co-workers[5] has focused on solvation of *n*-BuLi in THF. Very recently (May 2017) they published an article where they claimed to characterise the solvation state of *n*-BuLi (Figure 4.1); the solvation state is primarily a tetra-solvated tetramer (major species) in equilibrium with the tetra-solvated dimer deaggregate (minor species).



$2[(n\text{-BuLi})_2\cdot 4\text{THF}] \rightleftarrows (n\text{-BuLi})_4\cdot 4\text{THF} + 4\text{THF}$

Figure 4.1. Thermodynamic equilibrium system of *n*-BuLi oligomers in THF solution. Structures were subjected to NMR modelling at the B3LYP_GD3/6-311++G(d,p) level of theory.

With the computational modelling conducted in Chapter 3, both the tetra-solvated tetramer and dimer structures have been optimised and found to be the most probable equilibrium structures. With the success of optimising the mixed-aggregates, the next logical step is to generate theoretical NMR spectra to provide synergy between theoretical and experimental findings. Although computational NMR spectra may be generated with molecular modelling software such as Gaussian09,[6] are the results accurate enough to serve as a viable application to address such common problems encountered in organic chemistry? The answer is auspicious yes, as it has been reported in a recent review by Lodewyk, M.W and co-workers,[7] that not only is computational NMR applicable to research, but the field has seen an increase in accuracy and affordability due to growing interest and publications.

Reported spectra for the oligomers of *n*-BuLi comprise 1-dimensional (1-D), 2-dimensional (2-D) and diffusion-order (DOSY) NMR,[2,5] but Gaussian09 can theoretically only generates 1-D NMR. Despite that limitation, the literature does well to correlate 1-D with that of 2-D and DOSY NMR.[5] Therefore, comparison of theoretical and experimental 1-D NMR is acceptable for confirming the structural species of *n*-BuLi in THF.

4.3. Experimental Procedure

A 0.60 ml aliquot of commercially obtained deuterated tetrahydrofuran (7.37 mmol, THF-d_8) was transferred to an NMR tube via a 1 ml syringe equipped with a thin capillary needle. The NMR tube was then transferred to an acetone/dry-ice cold bath prior to the addition of 0.05 ml commercial solution of *n*-BuLi in hexane (0.55 mmol,11 M). Transfer of the *n*-BuLi required a constant flow of argon into the sure/seal bottle containing the highly concentrated *n*-BuLi, while the syringe and NMR tube were prepared in an inert atmosphere using argon. Note: due to the cold environment in which the sample was prepared, highly concentrated *n*-BuLi underwent a solid phase transition (freezing point of *n*-BuLi: –76 °C) upon contact with chilled THF-d_8. This was rectified by heating up the sample slightly and allowing THF-d_8 to progressively dissolve *n*-BuLi. The mole ratio of ca. 1:13 for *n*-BuLi to THF-d_8, ensured that the tetra-solvated dimer would be present in the NMR spectra, as the literature suggests a ratio larger than 10.[5c] Unless otherwise stated, all 1-D NMR were acquired on a 400 MHz Bruker AVANCE III spectrometer (^{1}H 400.13 MHz, ^{13}C 100.61 MHz & ^{7}Li 155.51 MHz). ^{1}H and ^{13}C chemical shifts were referenced internally to that of THF-d_8 at 3.58 (or 1.73) ppm and 67.57 (or 25.37) ppm respectively. Lithium bromide (LiBr) in deuterated water (D_2O) at 0 °C (273.15 Kelvin) served as an external reference for all ^{7}Li chemical shifts. Attempts at reproducing reported spectra involved running 1-D NMR at –40 °C. In addition, ^{1}H and ^{7}Li NMR spectra were obtained at temperatures; 0 °C, –10 °C and –60 °C.

4.4. Computational Details

With any computational modelling NMR, the first thing to consider is what sources of error may arise and how to address them. Common errors generally emanate if electron correlation, solvent interaction, conformational and heavy-atoms effects are not taken into consideration. Electron correlation is best described as the electron-electron instantaneous interactions. If neglected or incorrectly modelled, the result thereof is an inaccurate description of the electron density and nuclei shielding constants, which are required for determining chemical shifts. Solvent interaction is simply modelling the true molecular system, so for any solution system solvent effects should be introduced or else geometries and shield constants may be inaccurate. NMR modelling is always performed on a single structure, so the molecule might as well be the LEC which theoretically contributes significantly towards the experimental spectra. For the structures in Figure 4.1, the mentioned sources of error have been dealt with, as each structure was acquired by implementing a conformational search protocol, which included applying a solvation model along with empirical dispersion-corrections (refer to Chapter 3).

Heavy-atom effects relate to lighter atoms bonded to halogen atoms and atoms from the third row or the periodic table onwards, where the error originates from the neglect of relativistic effects. The error produced is reported as above average, and usually, the calculated chemical shifts are deshielded (downfield) in comparison to experimental. The latter should not be a concern for species found in Figure 4.1 but may be in effect when concerning reference molecules such as lithium bromide in heavy water.

4.4.1. NMR: Molecules of Interest & Reference Compounds

Theoretical NMR were generated utilising the B3LYP_GD3/6-311++G(d,p) level of theory, along with the Gauge-Independent Atomic Orbital (GIAO)[8] method as implemented in Gaussian 09 Revision D01.[6] NMR modelling was carried out on the LECs for each solvated oligomer (dimer & tetramer) of *n*-BuLi, refer to Chapter 3.

For each theoretical NMR spectra generated, the individual nuclei of the molecule of interest have unique isotropic shielding constants (σ_i), which must be converted to a chemical shift (δ) by subtracting σ_i from some equivalent nuclei type from a reference molecule (σ_{ref}):

$$\delta = \sigma_{ref} - \sigma_i \tag{4.1}$$

Experimentally, this is achieved by ^{1}H and ^{13}C NMR by using the most common reference standard; tetramethylsilane (TMS). With computed NMR, determining reference isotropic shielding constants require the same level of theory and protocol as implemented for generating each molecule of interest. In addition, silicon is considered a heavy atom and the possible error induced could affect chemical shifts. Considering that silicon may induce heavy-atom effects, an alternative reference compound is preferable as there are no real significant implications to and the possibility of error may be avoided. From literature,[7] it is known that for deuterated solvents, the experimental internal referencing procedure requires that assigned chemical shifts be relative to TMS (standard). Considering the experimental work employed THF-d_8 as an internal reference, the already modelled LEC of THF was an obvious choice for referencing theoretically computed ^{1}H and ^{13}C chemical shifts.

Now that a suitable reference molecule has been selected, one can convert chemical shifts computed in a manner that is analogue to experimental NMR by using the equation suggested by Lodewyk, M.W and co-workers.[7];

$$\delta_i = \sigma_{ref} - \sigma_i + \delta_{ref} \tag{4.2}$$

where δ_i is the chemical shift pertaining to each nucleus in the molecule of interest relative to TMS. This is calculated by using the shielding constants computed for the reference molecule (σ_{ref}), computed shielding constants from the molecule of interest (σ_i) and adding the experimentally determined chemical shifts for the reference molecule (δ_{ref}), relative to TMS. For deuterated THF, δ_{ref} is equal to 3.58 (or 1.73) ppm and 67.57 (or 25.37) ppm for ^{1}H and ^{13}C chemical shifts, respectively. The term σ_{ref} was obtained by computing the NMR spectra for the LEC of THF. The average computed shielding constants obtained for THF are; 28.01 (or 30.07) ppm and 110.07 (or 152.61) ppm for α-^{1}H (or β-^{1}H) and α-^{13}C (or β-^{13}C), respectively. Refer to the Supporting Information, Appendix B.

Unfortunately, Eq. 4.2 cannot be applied to ^{7}Li NMR as the major drawback with lithium NMR is the lack of an agreed NMR reference standard. This means that although ^{1}H and ^{13}C chemical shifts can be referenced internally with respect to TMS, ^{7}Li does not have an internal experimental reference with which to determine chemical shifts. The usual experimental approach involves external referencing with that of either lithium chloride (LiCl) or LiBr in D_2O, where computing such reference compounds is susceptible to the heavy-atom effect. Though equation 4.2 may not be applicable to calculating computed ^{7}Li NMR, one can still use equation 4.1 in attempting to reproduce experimental behaviour and positioning of chemical shifts. The reference molecule LiBr was optimised using a HSM ($6D_2O$ explicit molecules), where the isotropic shielding constant correlates to 92.94 ppm. Refer to the Supporting Information, Appendix B.

Please note, computational NMR produced in Gaussian09 is not influenced by temperature.[6]

4.5. Results and Discussion

4.5.1. ^{1}H NMR

With any experimental NMR data, unanticipated chemical shifts will be present. This is no exception to the ^{1}H NMR spectra generated for *n*-BuLi (Figure 4.2). The peaks appearing further downfield from THF-d_8 at 4.86 to 4.94 and 5.82 ppm correlate well with the appearance of an alkene. Further investigation showed that *n*-BuLi can undergo thermal decomposition,[9] whereby β-hydride elimination occurs producing 1-butene and lithium hydride;

$$C_4H_9Li \rightarrow LiH + CH_2^{(1)}{=}CH^{(2)}CH_2^{(3)}CH_3^{(4)} \qquad (4.3)$$

The multiplet and triplet at 2.01 and 0.95 ppm, respectively, correspond to the hydrogens positioned furthest from the double bond in the 1-butene by-product. At 0.17 ppm on the ^{1}H NMR spectra, there is a singlet, at first, this was believed to be the hydrogen pertaining to LiH, but height and integration suggest that the peak belongs to an impurity. The chemical shifts at 0.86 and 1.24 ppm fit to hexane solvent present and correspond with literature (0.89 and 1.29 ppm, respectively).[10] The remainder of the ^{1}H NMR chemical shifts belongs to that of *n*-butyllithium, where literature reports *n*-BuLi existing as a tetramer in equilibrium with a dimer in THF.[2a,b,5] In addition, the authors state that as the temperature of the system decreases, the equilibrium species are altered resulting in an increase in the proportion of the minor species (dimer) generated. Therefore, at –10 °C the ^{1}H NMR spectra represents chemical shifts solely for the tetrameric species. Due to the electron-rich lithium shielding the neighbouring hydrogens, the peaks corresponding to the α-hydrogens are found at –1.06 ppm (triplet, 2H). Further downfield at 0.80 ppm another triplet (3H) is observed for the δ–hydrogens furthest away from oligomer centre. The inner-chain β– and γ–hydrogens are found at 1.37 and 1.16 ppm (multiplet, 2H) respectively. A comparison of the ^{1}H NMR spectra at –10°C with those generated at –40 and –60°C indicates that the spectra are almost identical, but closer

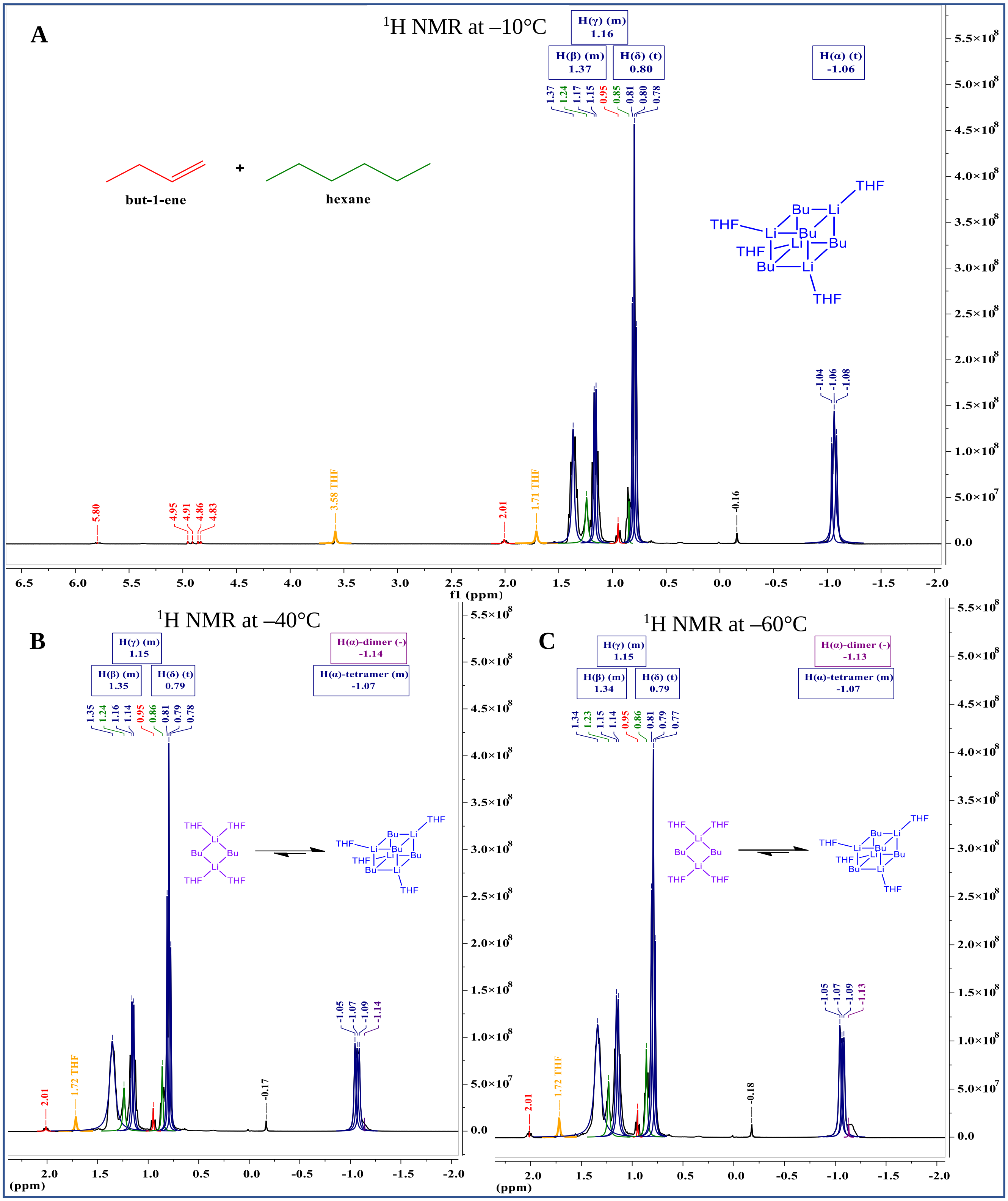


Figure 4.2. 1D experimental ^{1}H NMR spectrum of *n*-BuLi in THF-*d*$_8$. (A) ^{1}H spectrum at –263.15 K, labelled butyl resonance of tetrameric *n*-BuLi species and by-product resonance of 1-butene. (B) Section of the ^{1}H spectrum at –233.15 K, labels include the almost resolved α–CH$_2$ group of the *n*-BuLi dimer. (C) Section of the ^{1}H spectrum at –213.15 K.

inspection shows that a dimer is present. This is evident at ca. –1.13 ppm where a new peak is observed upfield to the tetramer. In addition to this, the peaks corresponding to the α–, β– and γ–hydrogens are less resolved in terms of splitting due to the overlapping of equivalent dimer hydrogens with that of the tetramer. With the elucidated experimental ^{1}H NMR spectra, how does computational generated NMR spectra compare?

The two ^{1}H NMR spectra generated in Figure 4.3 correlate to utilising the two computed shielding constants (σ_{ref}) from the THF reference molecule. Figure 4.3A correspond with using the α–

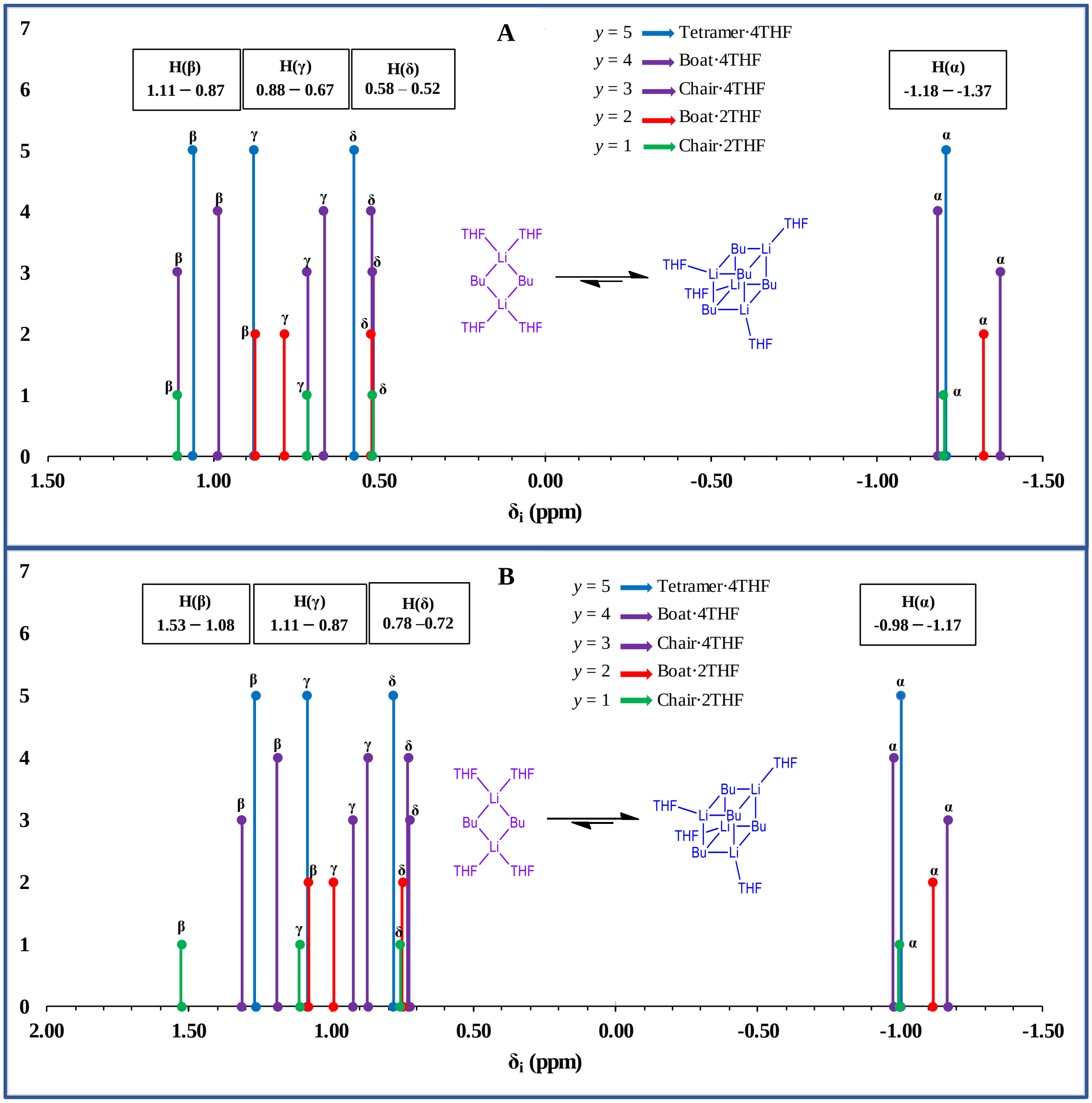


Figure 4.3. 1D computed ^{1}H NMR spectrum of *n*-BuLi, spectra include the average* chemical shifts for the butyl CH_n groups pertaining to the dimer and tetramer *n*-BuLi species. (A) Computed ^{1}H spectrum, utilising the average* α-CH_2 shielding constant for THF, σ_{ref} = 28.01 ppm. (B) Computed ^{1}H spectrum, utilising the average* β-CH_2 shielding constant for THF, σ_{ref} = 30.07 ppm. * Please refer to Supporting Information, Appendix B.

hydrogen shielding constant (σ_{ref} = 28.01 ppm), where the generated computed chemical shifts are further upfield in comparison to the shifts generated in Figure 4.3B by using the β–hydrogen shielding constant (σ_{ref} = 30.07 ppm). The increase in electron shielding of the predicted chemical shifts in Figure 4.3A is due to the α-hydrogens of the reference molecule being located adjacent to the highly electronegative THF oxygen. Therefore, the computed ^{1}H spectra; Figure 4.3B will serve as the comparison against experimental spectra.

First of all, the computed ^{1}H NMR data were useful in predicting the positioning of the various chemical shifts; the β–hydrogens are positioned downfield from the γ–hydrogens and the computed α–hydrogens situated upfield at ca. –1.00 ppm. When comparing the individual solvated aggregates, it is apparent that the chemical shifts belonging to the tetramer are generally downfield in comparison to most of the dimer species. The one major exception is that of the di-solvated chair conformation yielding downfield peaks for the β–, γ– and α– in comparison to the tetramer. Another exception is that of the tetra-solvated chair conformation yielding a downfield peak in relation to the tetramer. Importantly, similar behaviour is observed in the published NMR works by Keresztes and Willard,[5a] where the β–hydrogen chemical shifts allocated for the dimer is also located downfield in relation to the same β–hydrogen nuclei type for the tetramer. Computed NMR may have reproduced the positioning and to an extent the chemical shift values, but the generated spectrum is not picture-perfect. The chemical shifts belonging to the β–, γ– and δ– hydrogens of the tetramer are experimentally more deshielded (downfield) than what is predicted computationally. Although this is the case, computational ^{1}H NMR accomplished what it was meant to do, which was to aid in interpretation of the experimental data and confirm the solution state of *n*-BuLi in THF to be tetra-solvated.

4.5.2. ^{13}C NMR

The absence of 1D ^{13}C NMR spectra in literature for *n*-BuLi was baffling, as numerous NMR studies have been published. Therefore, inquisitiveness and a desire for knowledge lead to the notion that it was imperative that a ^{13}C NMR spectrum is obtained. Having accomplished this, an analysis of the experimental ^{13}C NMR spectra generated at –40 °C made it clear as to why ^{13}C NMR spectra were perhaps not published, see Figure 4.4. The spectrum is ambiguous, as there are a greater number of signals than expected, which makes characterisation of the individual carbons pertaining to *n*-BuLi in THF-d_{8}, not an easy task at all. At least, from the experimental spectrum, the peaks at 141.11 and

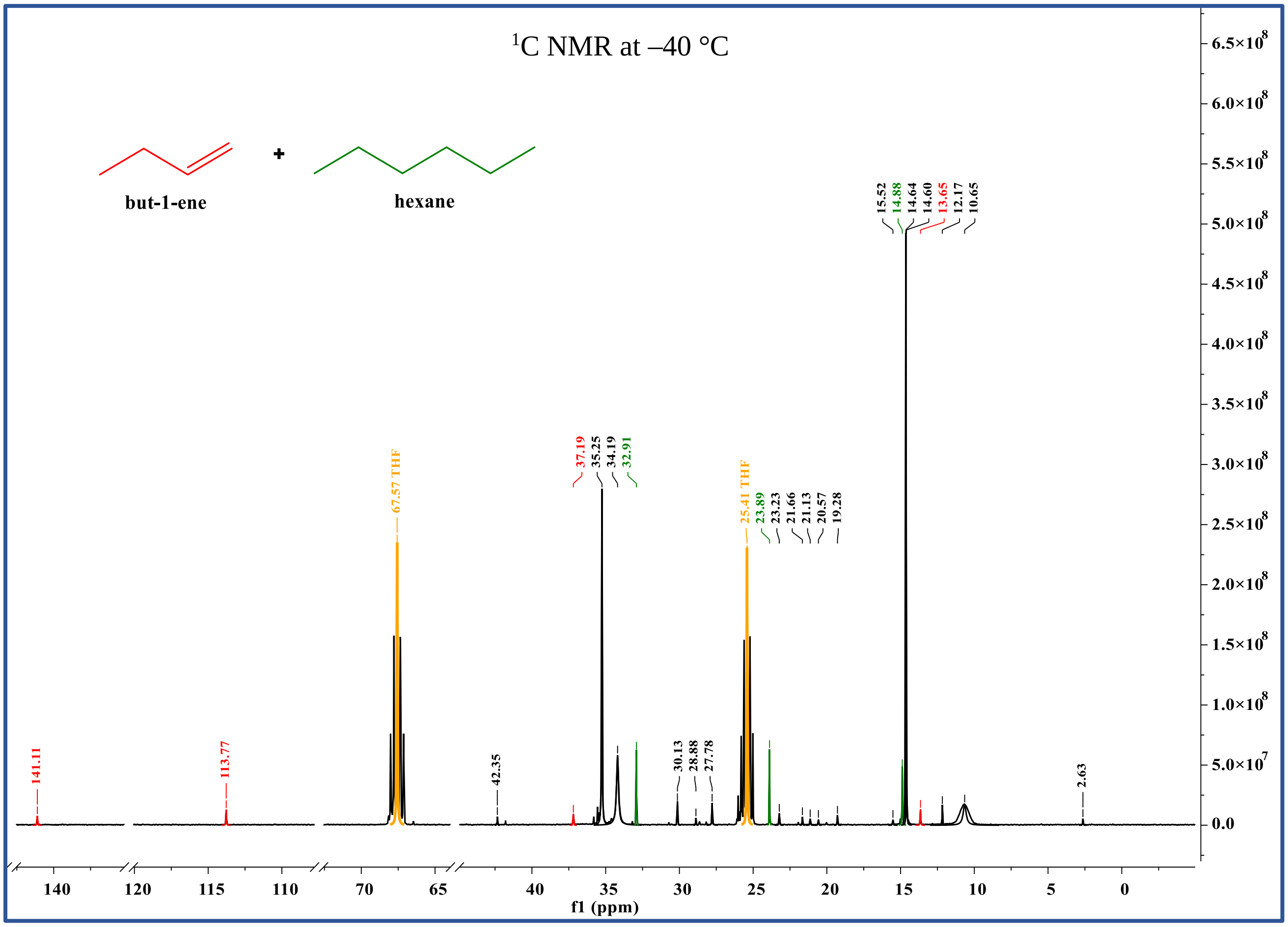


Figure 4.4. 1D experimental ^{13}C NMR spectrum of *n*-BuLi in THF-d_8 at – 233.15 K, with the labelled resonance of 1-butene and hexane.

113.77 ppm are characteristic of an alkene, which supports the ^{1}H NMR spectra for the presence of the 1-butene by-product. In addition, the chemical shifts at 37.19 and 13.65 ppm have been assigned to carbons $C^{(3)}$ and $C^{(4)}$ relating to 1-butene, respectively. Apart from the already labelled signals in Figure 4.4, the remaining ^{13}C shifts should correspond to the existing solution state species of *n*-BuLi. One would expect four distinct signals for the non-equivalent butyl carbons, however, there are greater than ten unique carbon signals, with two noticeable peaks at 35.25 and 14.64 ppm. Generally, the latter correlates with a CH_3 group while the former a deshielded CH_2 group, but due to not having four distinct carbon peaks with similar intensity, assigning the peaks is ambivalent. The data would then suggest possible ^{13}C signal overlapping relating to the carbons of *n*-BuLi, this is proposed by the computed ^{13}C NMR spectra found in Figure 4.5.

For each computed spectrum the most deshielded carbon belongs to the γ–carbon, followed by the β–carbon, then δ–carbon, leaving the α–carbon signals to be furthest upfield due to the rich electron environment. When comparing the dimer and tetramer carbon shift, it is observed that the tetra-solvated dimer peaks are either equivalent to the tetramer signal or downfield. Furthermore, computed β–carbon shifts relating to the tetra-solvated dimer overlap with the tetramer signal for the γ–carbon. Although overlapping may be possible, the resolution of the experimental ^{13}C NMR spectra can distinguish between carbons which have a resonance differing by ca. 0.5 ppm. Also, the computational NMR does not aid in identifying the small ^{13}C signals ranging from 19.28 to 30.13 ppm in the experimental spectrum. Therefore, Computational ^{13}C NMR is not applicable for

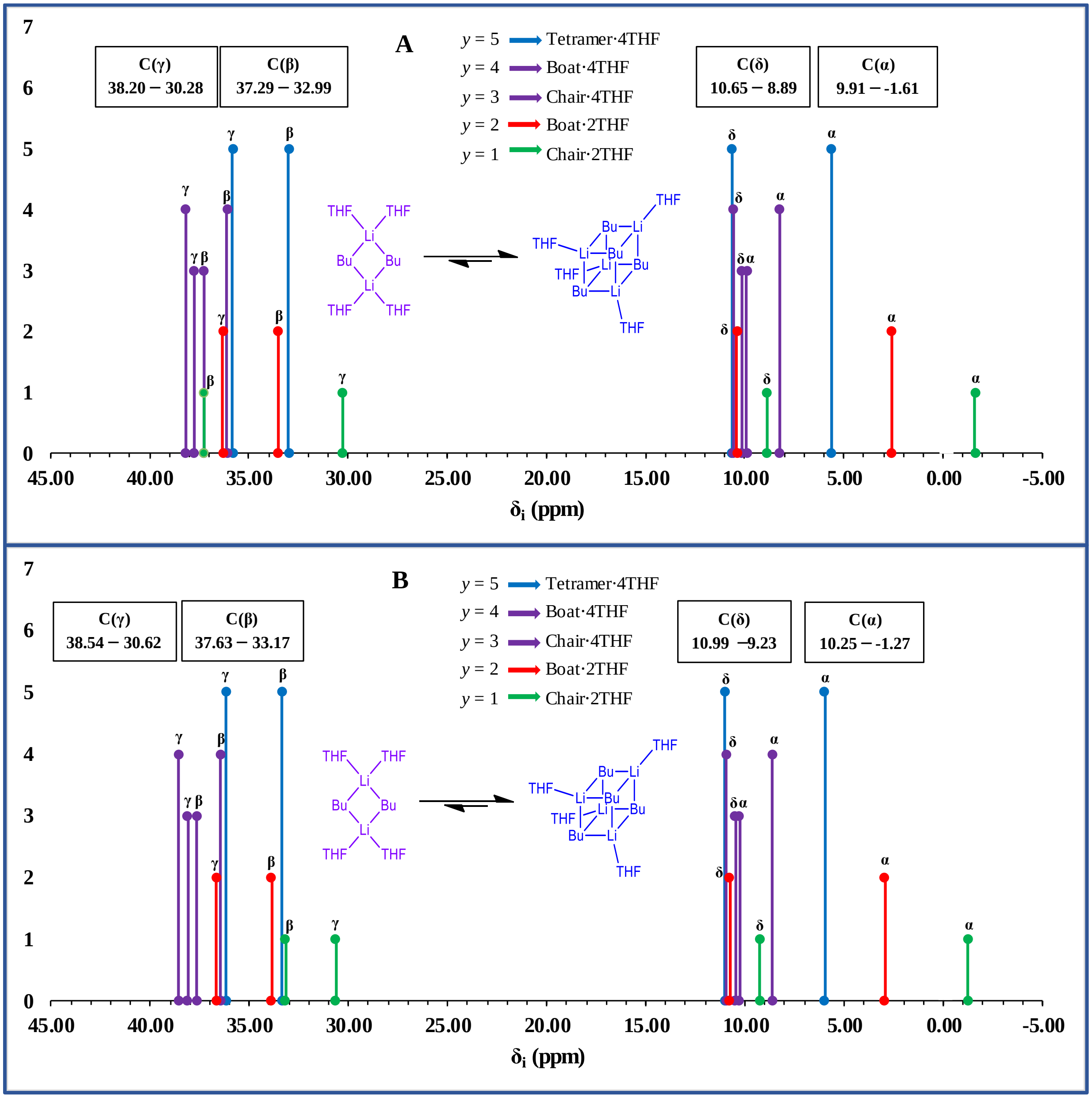


Figure 4.5. 1D computed ^{13}C NMR spectrum of *n*-BuLi, spectra include the average* chemical shifts for the butyl CH_n groups pertaining to the dimer and tetramer *n*-BuLi species. (A) Computed ^{13}C spectrum, utilising the average* α-CH_2 shielding constant for THF, σ_{ref} = 110.07 ppm. (B) Computed ^{13}C spectrum, utilising the average* β-CH_2 shielding constant for THF, σ_{ref} = 152.61 ppm. * Please refer to Supporting Information, Appendix B.

assigning carbons as the experimental data was not reasonably reproduced. Ways to possibly better quantify the spectra would be to generate ^{13}C NMR spectra at –10 °C to inhibit the dimer peaks for easier characterisation or select a higher level of computational theory for improved accuracy.

4.5.3. ^{7}Li NMR

Unlike ^{13}C, ^{7}Li NMR spectra are extensively published in literature as they tend to be unambiguous.[2d,5] Although this is the case, many authors have several contradicting spectra and results. In 2000, an article by Keresztes & Willard stated that the solution structure of *n*-BuLi in THF was well characterised.[5a] From the same literature, the ^{7}Li spectrum reported in the supporting information showed two resolved ^{7}Li singlets at –84°C, where the downfield peak was marked ‘D’ for dimer and the upfield labelled ‘T’ for tetramer. A few years later in 2006, the authors Qu and Collum published their ^{6}Li NMR spectra of *n*-BuLi in THF at –115°C,[2d] assigning the resolved downfield signal as a dimer and the upfield singlet as the tetramer. So far, no contradictions have been stated, but in 2011 a paper published by Kagan, Hopson & Willard reported ^{6}Li NMR spectra of *n*-BuLi in THF at –80°C.[5b] The spectrum contained three resolved singlets, where the furthest upfield singlet was labelled $(n\text{-Bu}^{6}\text{Li})_2(\text{THF})_4$ indicating dimer, the most intense signal situated in the middle was labelled tetramer and the downfield singlet was neither labelled nor mentioned in the literature. Due to having contradicting results from three different articles, it is imperative that ^{7}Li NMR spectra for *n*-BuLi in THF be obtained experimentally at various temperatures to confirm the true spectroscopic behaviour, see Figure 4.6.

Spectrum 4.6A was generated at 0°C, where only one singlet is observed at 1.09 ppm for the lithiums present, this corresponds to the solvated tetramer. Then at –10°C (spectrum 4.6B), the tetramer singlet remains, but a small unresolved peak appears upfield at 0.58 ppm, this is characteristic of dimer formation due to the lower temperature of the system. Following further cooling of the system to –40°C (spectrum 4.6C), a distinct resolved dimer singlet is observed at 0.40 ppm. The last spectrum (4.6D) was obtained at –60°C, and in addition to the resolved tetramer and dimer peaks at 1.08 and 0.4 ppm, respectively, an unresolved signal at 1.46 ppm is observed. The latter experimental spectrum resembles the reported ^{6}Li NMR spectrum of *n*-BuLi in THF at –80°C,[5b] where three lithium signals were observed. Although a third downfield peak appears in the spectrum, assigning it may be futile as it may resemble either a conformational change (boat/chair), intermediate step relating to dimer–tetramer interconversion, or even a species containing a unique number of solvated THF. Hence, computational ^{7}Li NMR spectra were generated to assist in assigning and confirming the experimental data, see Figure 4.7. The first generated spectra, Figure 4.7A, was plotted by using equation 4.1 and the lithium shielding constant obtained from the optimised reference molecule; LiBr·6D$_2$O (σ_{ref} = 92.94 ppm), As expected the computed chemical shifts are largely deshielded due to the heavy-atom effect.[7] To overcome this, the computed ^{7}Li NMR spectrum was scaled to that of the experimental spectra, where the computed chemical shift of the tetramer was adjusted to the value 1.09 ppm, which is equivalent to the experimental. The result thereof is displayed in Figure 4.7B and it is noticeable that the tetra–solvated dimer is located upfield from that of the tetra-solvated tetramer. This behaviour supports the literature and agrees with the experimental spectra on the positioning of the tetra-solvated dimer peaks.[5b] For the di-solvated dimer species of *n*-BuLi, it is observed that the chair conformation species is greatly deshielded and

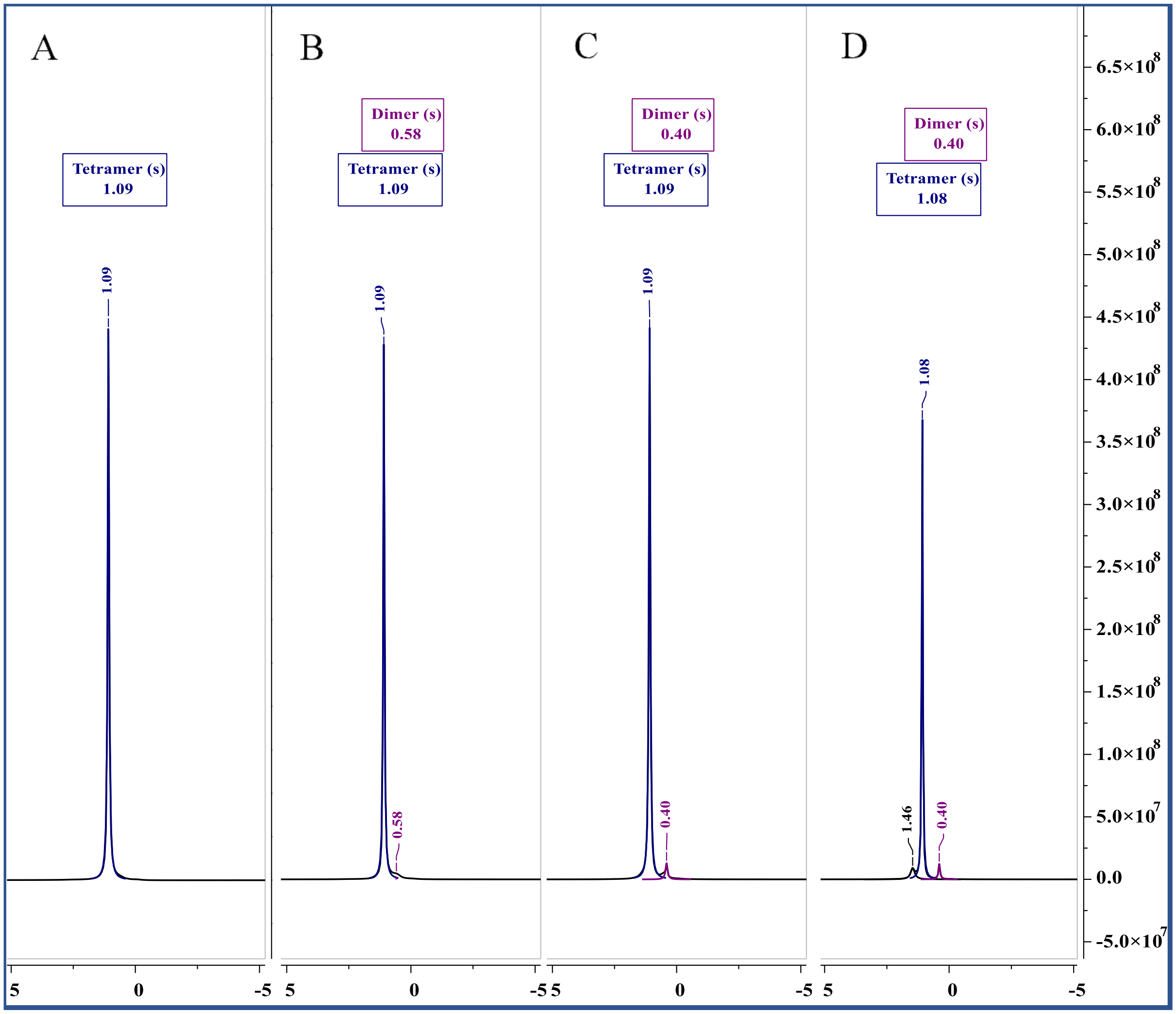


Figure 4.6. 1D experimental ^{7}Li NMR spectrum of *n*-BuLi in THF-d_8. (A) ^{7}Li spectrum at – 273.15 K, labelled lithium resonance of tetrameric *n*-BuLi. (B) ^{7}Li spectrum at – 263.15 K, labels include the almost resolved *n*-BuLi dimer (C) ^{7}Li spectrum at – 233.15 K, resolved lithium resonance for both tetrameric and dimeric *n*-BuLi species. (D) ^{7}Li spectrum at – 213.15 K.

yields a lithium signal found downfield at 1.30ppm, whereas the boat conformation is upfield at 0.96 ppm. Although the di-solvated chair species lies to the left of the tetramer, the peak is not dieshielded enough to resemble the experimental shift at 1.46 ppm. Therefore, it is safe to say that the ^{7}Li signal at 1.46 ppm is neither a unique dimer conformation nor a di-solvated *n*-BuLi species. It is best to propose that the downfield peak correlates with an intermediate species, such as the tetramer undergoing dissociation. In order to assign the peak to a true structural species, further investigation is required.

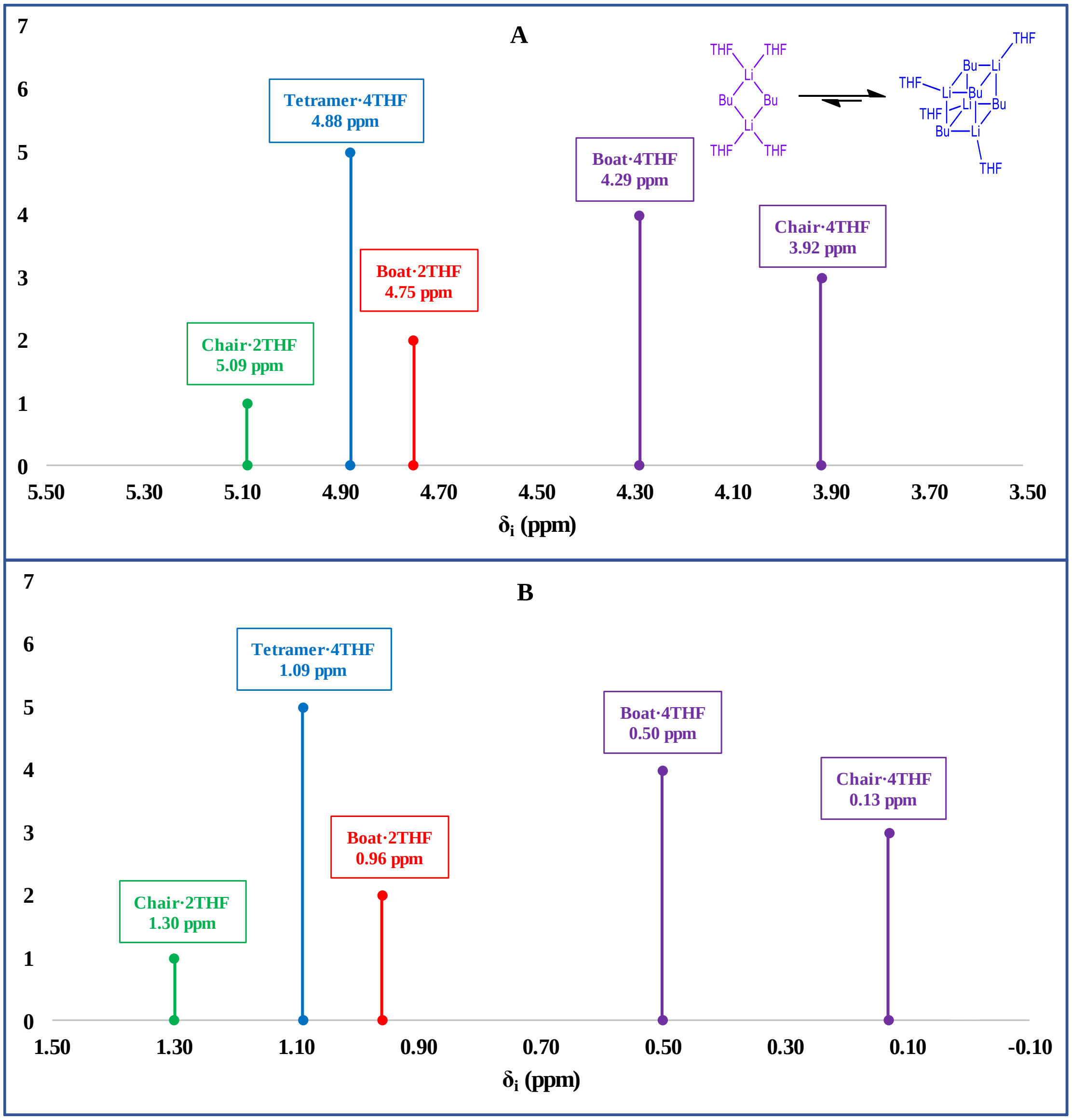


Figure 4.7. 1D computed ^{7}L NMR spectrum of *n*-BuLi, spectra include the average* chemical shifts for the lithium atoms pertaining to the dimer and tetramer *n*-BuLi species. (A) Computed ^{7}L spectrum, utilising the Li shielding constant for LiBr – 6D$_2$O, σ_{ref} = 92.94 ppm. (B) Computed ^{7}L NMR spectrum by normalising the computed tetramer peak to 1.09 ppm. * Please refer to Supporting Information, Appendix B.

4.6. Conclusion

The theoretical computational model presented in this body of work generated fairly accurate qualitative one-dimensional spectra. Furthermore, the theoretical ^{1}H and ^{7}Li NMR data have successfully aided in assigning chemical shifts and confirmed the equilibrium mixed–aggregation of *n*-BuLi in THF. There is no doubt that the two aggregates species observed in the experimental NMR are that of the dimer and tetramer. Furthermore, these data showed that each oligomer is tetra-solvated. Assignment of chemical shifts for individual nuclei for the experimental ^{13}C NMR is not possible, but theoretical NMR has confirmed that the uncertainty is perhaps due to an overlap of nuclei with equivalent chemical shifts. Lastly, it has been shown that the dimer to tetramer ratio is influenced by the temperature of the system, where the proportion of dimer increases as the temperature of the system is lowered. This behaviour can be observed by the four reported experimental ^{7}Li NMR spectra obtained at various temperatures.

4.7. References

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Chapter 5

Reaction Mechanism of Solvated n-Butyllithium with Halogenated Thiophene

5.1. Abstract

DFT computation study on the reaction mechanism of *n*-BuLi with mono-halogenated thiophene in THF, involving two unique solvation models, is reported for the first time. The results show that overall bromine has favourable reactivity over chlorine as the generated TSs along the reaction energy profile is significantly more stable. From the characterisation of the TSs, it has been confirmed that the reaction mechanism does indeed involve the formation of the ate-complex suggested previously. Furthermore, the stability of the ate-complex is dependent on how well the halogen can accommodate a negative charge and the degree of lithium interaction. Lastly, each solvation model adequately defined the reaction profiles for all computed lithium-halogen exchange reactions.

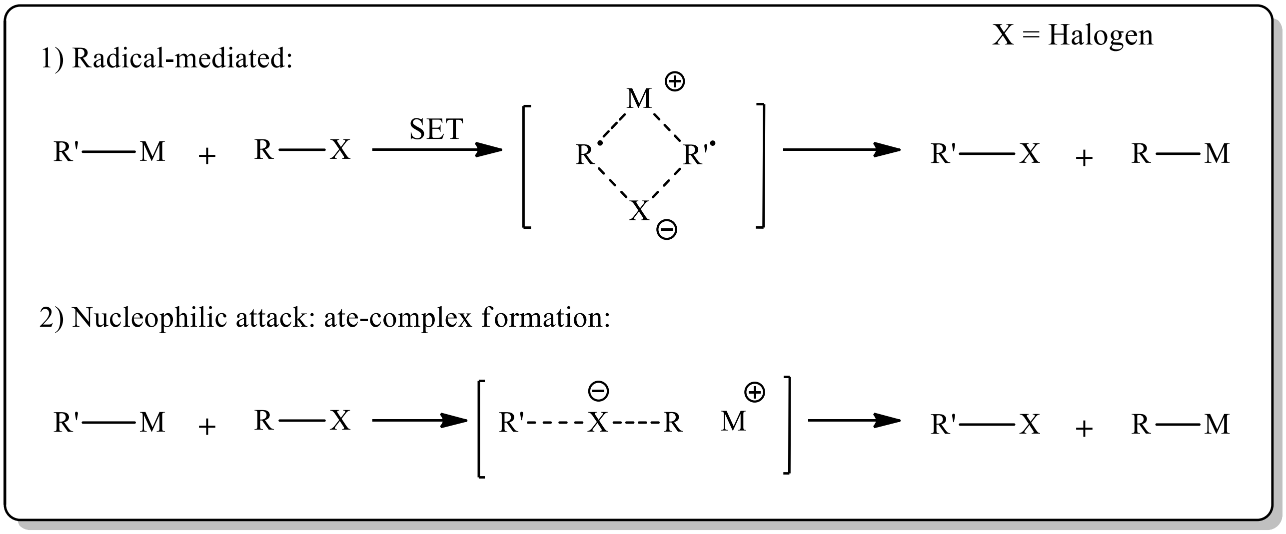
Furthermore, an investigation on the structural behaviour of the products (lithiated thiophene) was conducted. This work has been shown that thiophene, as an organolithium reagent, favours a homodimer equilibrium geometry in THF solution and that the lithium situated at the alpha position is more stable.

5.2. Introduction

Lithium–halogen exchange is a reversible organic chemistry reaction discovered in the late 1930s by Wittig and Gilman.[1,2] The reaction favours the organolithium species which better stabilises the negative charge on the α-carbon (R/R^1) bonded to the lithium:

$$R—Li + R^1—X \rightleftharpoons R—X + R^1—Li \tag{5.1}$$

This reaction and the mechanism thereof has been the subject of numerous studies,[3–6] and two key certainties have arisen from these studies; the exchange reaction is dependent on both the reactive structure and reaction conditions (i.e. temperature).[3] Computational chemistry is a technique that affords one the opportunity to study both the geometry and simulate reaction conditions.[6] We know that there are several proposed mechanisms for describing the reaction in question. However, only two of the proposed mechanisms have supporting evidence, see Scheme 5.1. The first is the radical-mediated mechanism (single electron transfer—SET)[4,5a] and the second, nucleophilic attack of the organolithium with the halogen to form an ate-complex (a Lewis acid combines with a Lewis base whereby the central atom (from the Lewis acid) increases its valence and gains a negative formal charge) intermediate/transition state (TS).[4,5b]



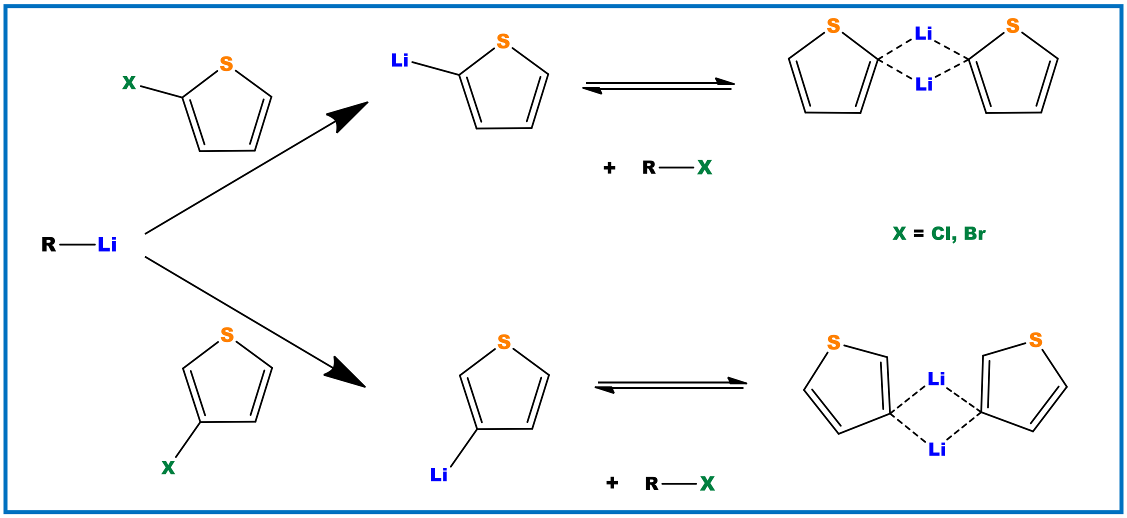
Scheme 5.1. Proposed mechanistic schemes for halogen–metal exchange.

Mechanistic efforts relating to possible SET pathways have been done and radicals are sometimes observed,[4,6a–b] but, often the radicals observed are reported as side reactions or are inconclusive. Ate-complex formation, on the other hand, is suggested to be the fundamental step for all lithium-exchange reactions due to structural and spectroscopic characterisation studies.[3]

Furthermore, it is said that homolytic moiety within an ate-complex could account for the observation of radical intermediates.[6b]

The existence of ate-complex species and the negative (anionic) halogen bonded to carbon is evidenced in literature. However, full characterisation of such structures is uncommon due to their highly reactive nature.[3-6]

The work herein focuses on using computational chemistry to model the unequivocal Li–halogen exchange reactions between solvated *n*-BuLi and the mono-halogenated thiophene (heterocyclic compound). Solvated *n*-BuLi was structurally identified and supported by literature as detailed in Chapters 3 and 4, which leaves the monosubstituted heterocyclic thiophene structures to be modelled and their lowest energy conformer (LEC) to be identified. Two different halogens were utilised in the reactions, chlorine (Cl) and bromine (Br) so that it is possible to measure and compare the reactivity of each. The accepted reaction rate of any lithium-halogen exchange reaction is dependent on the halogen present, which conventionally is as follows; I > Br > Cl. An analysis of the literature[3] shows that not only does *n*-BuLi exist as a mixed–aggregate, but also the thiophene organolithium reagents, whereby instead dimer–tetramer, one finds both the monomer and dimer species to exist, see Scheme 5.2.



Scheme 5.2. Proposed lithium-halogen exchange reaction between an organolithium reagent (R–Li) plus the alpha (α) and beta (β) mono-halogenated species of thiophene.

The study of the reaction mechanism of solvated *n*-BuLi with the monosubstituted heterocycle focused on the identification of the products, transition states (TSs) and an evaluation of whether or not the popular ate–complex plays a role in the reaction mechanism.

5.3. Computational Details

5.3.1. Transition State Protocol

Finding a TS is by no means an easy task, especially when computing for large systems, which include electronically dense elements such as bromine. Locating the TSs first involved establishing the optimum approach for the Li—Br exchange to occur. This involved implementing potential energy surface (PES) scans in Gaussian, whereby the LEC reactants are placed within proximity and then a scan coordinate calculation allows each reactant to approach one another to hopefully induce an exchange reaction. From the numerous scans, the most favourable method for the reaction to take place was allowing the halogen to approach the α-carbon, as seen in Figure 5.1.

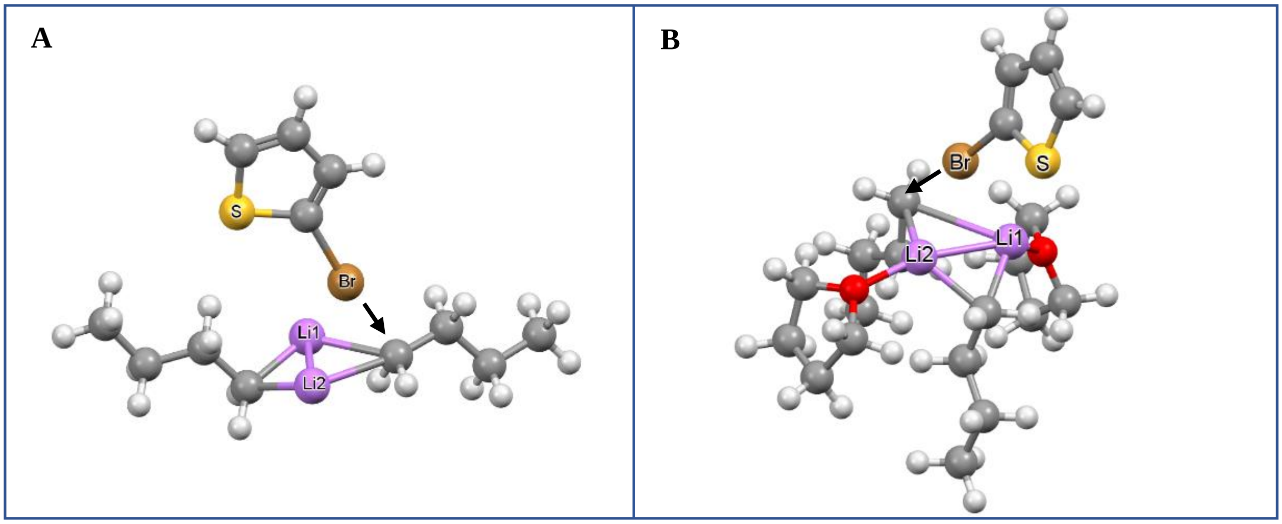


Figure 5.1. Optimum geometry found for mono-halogenated 2-bromothiophene to approach the anionic α-carbon of *n*-BuLi in either the CSM (A) or HSM (B).

Furthermore, from the PES it was observed that the reaction proceeds when the mono-halogenated thiophene was placed within ± 2.5 Å of the α-carbon (Br– – –C_α). Therefore, to obtain TSs, the halogen was placed c.a. 2.5 Å from that of the *n*-BuLi α-carbon. The modified system was optimised using the Berny algorithm GEDIIS,[8] to generate plausible TS structure which should be first-order saddle points. All TSs were obtained using the dispersion corrected (GD3) UB3LYP-GD3/6-311++G(d,p) level of theory in conjunction with the default settings of the polarisable continuum solvation model (PCM) using THF as solvent (ε =7.4257).

Lastly, the PES scans computed generate possible thienyllithium products. These structures were optimised using the dispersion corrected (GD3) RB3LYP-GD3/6-311++G(d,p) level of theory in conjunction with the default settings of the polarisable continuum solvation model (PCM) using THF as a solvent.

5.3.2. Thermodynamic & Activation Terminology

As reported in Chapter 3, one can report on the thermodynamic data relating to equilibrium parameters for the reactions at -78 ˚C. In addition, it is possible to calculate and report the activation parameters for each reaction. To do this, one requires a TS which includes one imaginary frequency (first-order saddle point) and a vibrational mode that corresponds to a TS structure linking two minima (the desired products and reactants). Once such a structure is obtained, one can then report on the different energies of activation. The first activation energy term to report is the Gibbs free energy of activation ($\Delta G^{\ddagger}$):

$$\Delta G^{\ddagger} = \sum G_f^{TransitionState} - \sum G_f^{Reactants} \tag{5.2}$$

The equation is an indication of the rate of a chemical reaction. The greater the value for $\Delta G^{\ddagger}$ (positive value), the greater the energy required from the environment for the chemical reaction to occur. Furthermore, the rate can be quantified by the rate constant (k) which is estimated from $\Delta G^{\ddagger}$ using the modified "Eyring-Polanyi equation":[9,10]

$$k = \frac{\kappa k_B T}{h} e^{-\Delta G^{\ddagger}/RT} \tag{5.3}$$

κ is the transmission coefficient, which will be assumed to be equal to one (unity). Therefore, the fundamental no-recrossing assumption of transition state theory holds, whereby all transition state species formed proceed directly to products and never revert back into reactants.[11] k_B and h are the Boltzmann's and Planck's constants. The equation is used in kinetics to describe the rate of a chemical reaction at a specific temperature (T). Eq. 5.3 is relatable to the empirical Arrhenius equation which is commonly utilised for determining the activation energy (E_a) of a reaction:

$$k = Ae^{-E_a/RT} \tag{5.4}$$

Although the crudest way to calculate E_a is by using the Arrhenius equation (Eq. 5.4), the main problem is approximating the pre-exponential factor A (fraction of molecules with kinetic energy ≥ E_a). As such, another way to calculate E_a is to obtain the reaction enthalpy ($\Delta H^{\ddagger}$), which is calculated as follows:

$$\Delta H^{\ddagger} = H_f^{TransitionState} - \sum H_f^{Reactants} \tag{5.5}$$

The reaction enthalpy is then related to the Arrhenius activation energy[11] for a gas-phase bimolecular reaction by:

$$\mathrm{E_a} = \Delta H^{\ddagger} + 2RT \tag{5.6}$$

Programs such as Gaussian, automatically add the thermal correction terms (RT) to all energies at the end of a frequency calculation. Therefore, the energy terms are thermally and zero-point vibrational energy (ZPVE) corrected.[11] Hence, E_a is directly approximated by taking the difference between the transition state and reactant enthalpies;

$$E_a = \Delta H^{\ddagger} = H_f^{TransitionState} - \sum H_f^{Reactants} \tag{5.7}$$

Error in reporting thermodynamic parameters for solution-phase reactions.

Gaussian09 computes all thermodynamic parameters based on the assumption that the system is an ideal gas.[12] Broad thermodynamic free-energy errors are therefore possibly generated when modelling for solution-phase reactions. This is part of the age-old problem; how to tackle the role and behaviour of the solvent ("solvent effect") while still utilising theoretical tools grounded in the gas-phase. The ideal solution would be the implementation of an external model that accounts for the position, structure, dynamics and properties of all surrounding solvent while maintaining a high level of theory. One such model would be to completely incorporate the reagents into a box of solvent, but that is beyond current computing resource capabilities. The alternative is the implementation of an implicit solvent model and possibly the addition of explicit solvent to generate a hybrid solvent model (Chapters 2 & 3).

This limitation for representing the true solvent dynamics in Gaussian09 suggests that the molecular entropy contribution to solvation free-energy is ignored. The recent works by Fang et al[13,14] have addressed such concerns and have undertaken the task of accurately calculating solvation free energies. To date, the authors introduced a new set of atomic radii for generating the solute cavity and, in addition, a solution-phase translational entropy contribution to all free-energies was implemented instead of the standard gas-phase translational entropy (Gaussian output). They have shown that the gas-phase translational entropy contributes significantly to the inaccuracy and as such must be corrected to produce valuable free-energies for calculating applicable equilibrium/activation terms.

It would have served as a valuable tool to implement free-energy corrections, such as those produced by Fang et al,[13,14] but unfortunately, acquisition of the requisite software and tools was not possible during the course of the reported studies. Therefore, due to the possible unreliability in reporting free-energies generated from Gaussian09, all generated reaction thermodynamic data will be reported herein. All thermodynamic energies and activation parameters presented in this chapter will be reported for T = –78 °C, unless stated otherwise.

5.4. Results and Discussion

5.4.1. Geometry Analysis: Halogenated–Thiophene.

The Conformational search protocol, as described in Section 3.3.2, was implemented for the alpha (α)– and beta (β)–halogenated species of thiophene. As predicted from the intrinsic aromatic and planar properties of thiophene, only one energy conformation was generated for each halogen species. This is confirmed by an electron diffraction study conducted by Harshbarger and Bauer,[7] which reports that the addition of chlorine or bromine at the α-position, only distorts the C_{2v} symmetry of the thiophene ring. Additionally, the study provides experimental results from two models for the structural characterisation of 2-chlorothiophene and 2-bromothiophene. Model A from the literature will serve as a reference to validate the computed structures.[7] Finding the ground state structures of the monosubstituted species was done using the dispersion corrected RB3LYP-GD3/6-311++G(d,p) level of theory in conjunction with the default settings for the polarisable continuum solvation model (PCM), using THF as the solvent (ε =7.4257). In Figure 5.2, the optimised ground state structures for the mono-halogenated species of thiophene are shown. Table 5.1 shows the computed geometry parameters for the α-halogenated structures with a comparison to experimental data; keep in mind that the average C–H bond length is reported. The computed parameters for the β-halogenated structures can be found in the Supporting Information, Appendix C. The results show that the observed and calculated bond distances for both 2-chloro- and 2-bromothiophene are within 0.05 Å. For 2-chlorothiophene the computed bond lengths are mostly overestimated and for 2-bromothiophene we have a greater number of bond lengths which are underestimated. One notable trend observed for the computed bond lengths, which is in agreement with the experimental results, is the observed C_5—S bond length which is shorter in comparison to the C_2—S bond. From the bond angles we find that for 2-chlorothiophene, we have better structural accuracy in terms of Δδ falling within 0.6° of the experimental results, whereas 2-bromothiophene has on average a Δδ = 1.5°. It must be noted that the experimental results are from gas phase electron diffraction, and the computed structures are theoretically modelled in solution. That been said one may conclude that the calculated trends and bond lengths are satisfactory, and for such a simple heterocycle structure it is rational to expect that the planar geometries do not differ significantly from that found in both the gas and solution phases. With reasonable α-monosubstituted thiophene structures, the β-monosubstituted structures should also be acceptable, although the comparison to experimental data would be ideal.

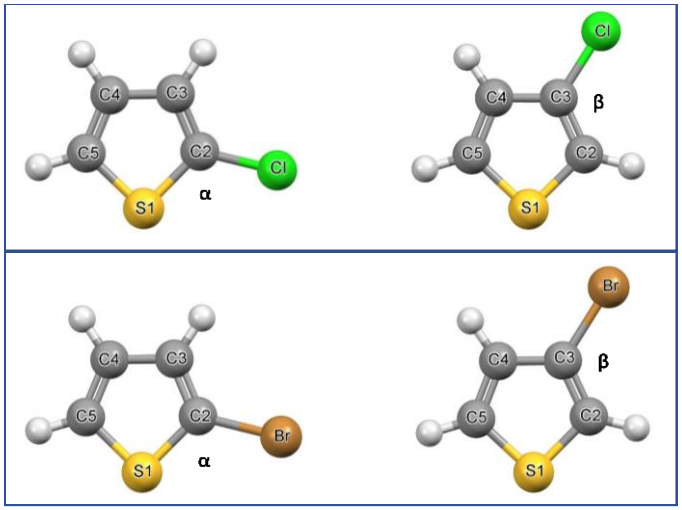


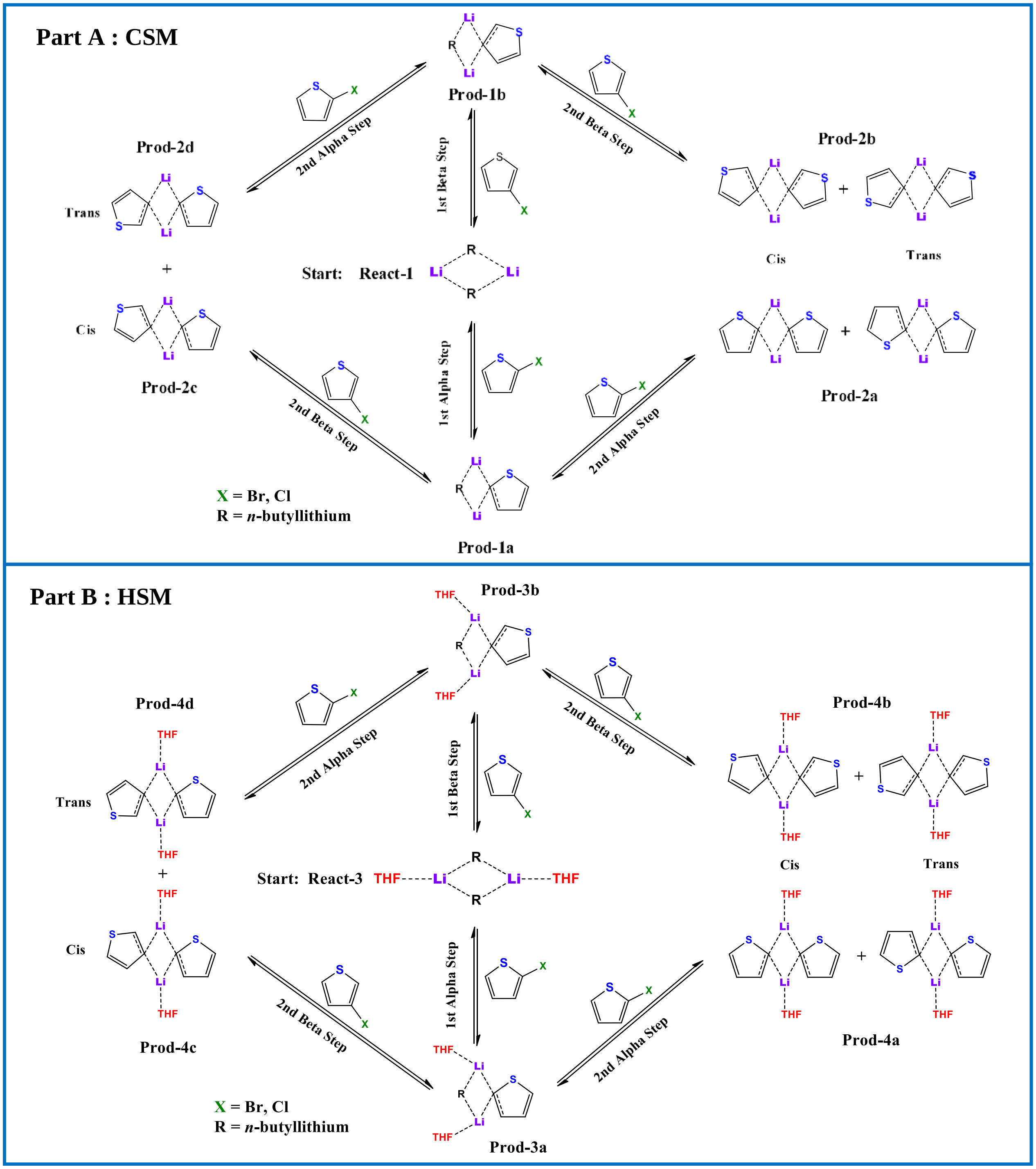
Figure 5.2. Ground state structures of the α & β halogenated-thiophene reactants.

Table 5.1. Comparison of the geometric parameters between the theoretical and experimental[7] data for 2-chloro- and 2-bromothiophene.

	C_4H_3SCl			**C_4H_3SBr**		
	Theoretical	**Exp.**	**Δδ**	**Theoretical**	**Exp.**	**Δδ**
Bond Lengths (Å)						
C(2)–S	1.743	1.727	-0.016	1.742	1.744	0.002
C(5)–S	1.739	1.715	-0.024	1.738	1.668	-0.070
C(2)–C(3)	1.364	1.391	0.027	1.365	1.39	0.025
C(3)–C(4)	1.365	1.398	0.033	1.428	1.464	0.036
C(4)–C(5)	1.429	1.359	-0.070	1.365	1.341	-0.024
C–H	1.081	1.073	-0.008	1.081	1.091	0.010
C(2)–X	1.737	1.713	-0.024	1.894	1.849	-0.045
Bond Angles (°)						
∠ CSC	90.5	90.8	0.300	90.7	92	1.300
∠ SC(5)C(4)	111.9	111.3	-0.600	111.8	114.7	2.900
∠ SC(2)C(3)	112.6	112.6	0.000	112.5	110.9	-1.600
∠ SCX	120.7	120.1	-0.600	121.0	120.7	-0.300

5.4.2. Reaction Energy Profiles.

And so, the reaction adventure begins. Twenty-four separate reactions were computed, these included the implementation of two separate solvation-models and four separate mono-halogenated species of thiophene reacting with two species of *n*-BuLi, as seen in Schemes 5.3.



Scheme 5.3. Organolithium stationary points generated from mono-halogenated thiophene and *n*-BuLi dimer, implementing both a CSM (A) and HSM (B).

There is a strong dichotomy between the continuum (CSM) and hybrid solvation models (HSM), as such each solvation model should be compared to aid in deciding which is ideal for modelling the system. Note the latter is the adopted model due to the added benefit of having explicit solvent interaction present, but the former is less demanding on resource and must not be thought of as inaccurate. Hence, the questions are whether one observes a significant qualitative contrast when modelling a chemical reaction adopting two solvation models?

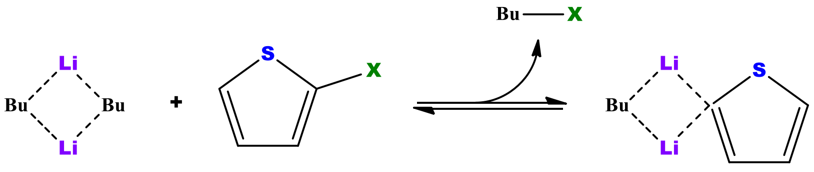
5.4.3. Reaction Energy Profiles: 1st step in alpha lithium-halogen exchange reactions

For each reaction, there are four parts; 1) the isolated reactants "**React**", 2) the reactant adducts "**Add**", 3) transition state "**TS**" and 4) the isolated products "**Prod**". The terminology; 'isolated' implies that each component that is associated with either the reactants or products, has been optimised independently. The reaction adduct was constructed by implementing a similar protocol as found in Section 5.3.1, whereby instead of defining the geometry optimisation to locate a first-order saddle point, a ground state structural geometry was located instead at the same level of theory.

When compiling the reaction profiles for part A of Scheme 5.3, the energies for the intermediate adducts, TS and products are relative to the starting reactants; [React-**1** + mono-halogenated thiophene]. It should be noted that the β-halogenated-thiophene is more stable relative to the α-halogenated-thiophene in terms of $\Delta G^{\ddagger}$ by –2.79 and –2.95 kcal mol^{-1} for bromine and chlorine, respectively.

Modelling using the Continuous Solvation Model (CSM)

Starting with the first alpha step reaction (***i***), two stationary points were located for the reaction profile in Figure 5.3; **Add–1a** and **TS–1A**. The adduct intermediate is qualitatively useful to measure the stability of the reactants when in close proximity. From the reaction profile, it is notable that the chlorine generated **Add–1a** is both non-spontaneous and endothermic in terms of relative free energies and enthalpy of formation, respectively. With regards to the bromine, the adduct is favourably more stable in comparison to chlorine and the relative reaction enthalpy (H_{rel}) indicates



React-1 **Prod-1a** **(*i*)**

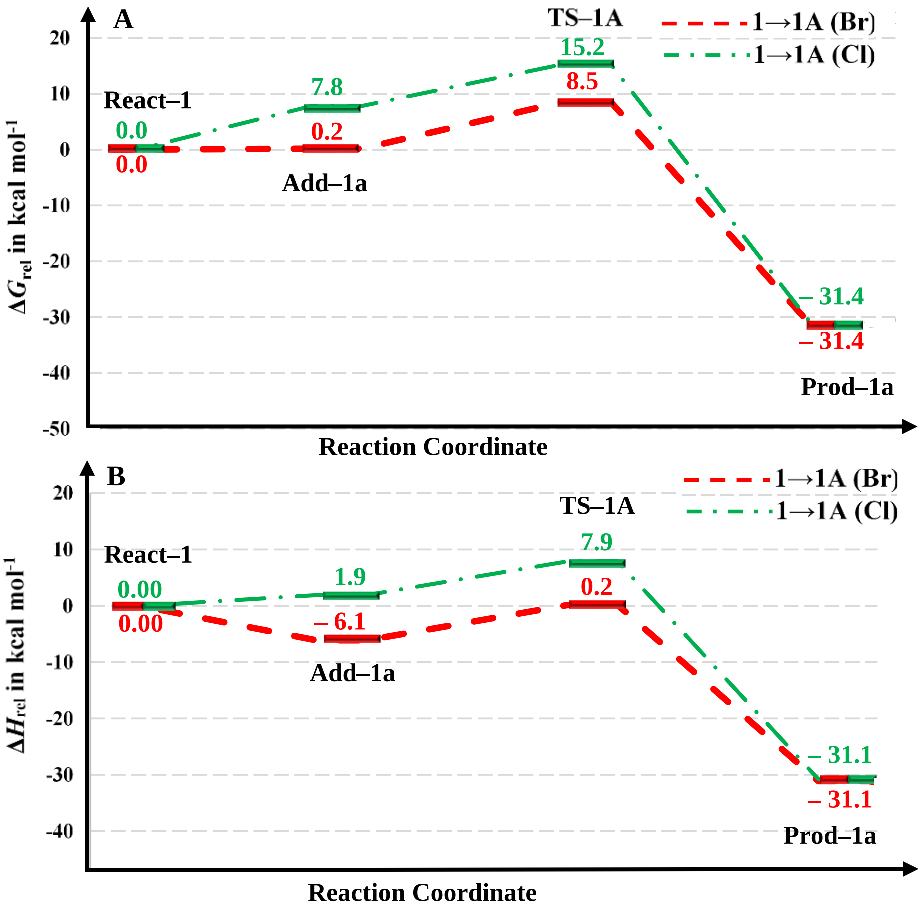


Figure 5.3. The reaction free energy (A) and enthalpy (B) profiles for the reaction **React–1** + 2–X–thiophene → **Prod–1a** at 195.15K. Refer to Figure 5.4 and Table 5.2 regarding structures.

that the adduct formation undergoes exothermic conditions (negative H_{rel}). Hence, the chlorine **Add–1a** stationary point reported here should rather be considered as not an adduct but rather a distinct molecular species that lies somewhere closer to the TS on the potential energy surface. The bromine adduct exhibits a behaviour (exothermic formation) that will be observed for all the remaining reaction adducts found in the energy profiles. Therefore, adducts will no longer be discussed in detail and the molecular structures and thermodynamic data can be found in the Supporting Information, Appendix C.

The next stationary point of interest is the transition state **TS–1A,** which involves the halogen attacking one of the anionic α-carbons. For the chlorine system, it is observed that the activation barrier is almost twice that of bromine, where the relative free-energies are 15.2 and 8.5 kcal mol^{-1}, respectively. When comparing H_{rel} it is found that the bromine system has an enthalpy barrier of 0.2 kcal mol^{-1}, which is insignificant in comparison to 7.8 kcal mol^{-1} for chlorine. This confirms the halogen-exchange trend that bromine has favourable reactivity over chlorine. If we compare the two

TS–1A structures found in Figure 5.4 pertaining to the reaction (***i***), it is possible to see the so-called bridging '10–X–2' ate complex,[3,5,6,8] where the anionic halogen interacts with two α–carbons. Furthermore, inspection of the bond lengths shows that there is no noticeable difference in the adjacent C(α)—S and C(α)—C(β) bond lengths of the thiophene ring. Although for the bond C(2)—C(β) belonging to the butane chain, the observed bond length of 1.524 Å is slightly shorter than the average bond length of 1.544 Å observed for the reactants. The most significant structural changes observed are that of the C(1)—X and C(2)—Li bond lengths, which have been stretched by over 10% (weaker bond interaction) to accommodate the halogen. For the **TS-1A** chlorine system, the halogen seems to be interacting primarily with a single lithium, signifying stability of the electronegative halogen before exchange occurs. For the **TS-1A** bromine system, the lithium atoms are exhibiting possible weak dispersion interaction with either lithium to accommodate the anionic charge, which proposes that the electron-rich bromine intrinsically generates a more favourable environment, hence the lower energy barrier. If one were to compare the results for reaction (***i***) with that of the equivalent HSM, what differences would be observed?

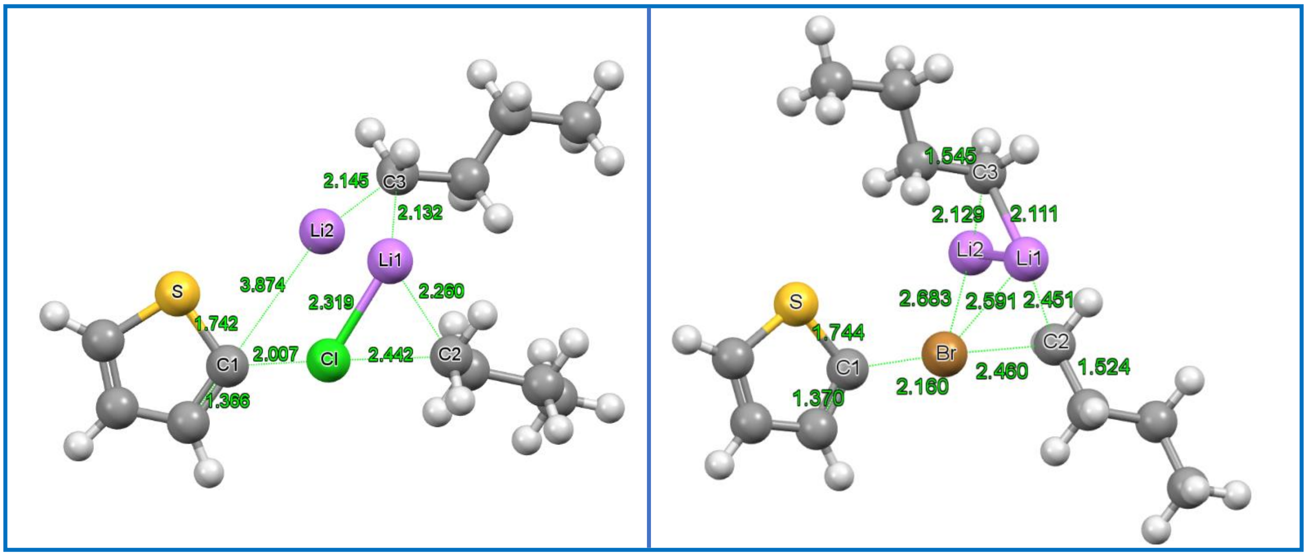
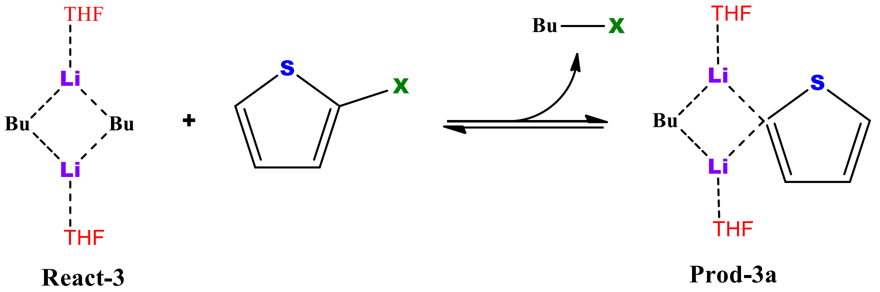


Figure 5.4. Optimised transition structures **TS–1A** for the reactions: **React–1 +** 2-Cl-thiophene → **Prod–1a** (A) and **React–1 +** 2-Br-thiophene → **Prod–1a** (B). Refer to the reaction energy profiles found in Figure 5.3.

Modelling using the Hybrid Solvation Model (HSM)

First of all, the first alpha step reaction system (***ii***) contains two explicit THF solvent, which means the *n*-BuLi dimer is more crowded in terms of spatial arrangement around the reactive α–



(ii)

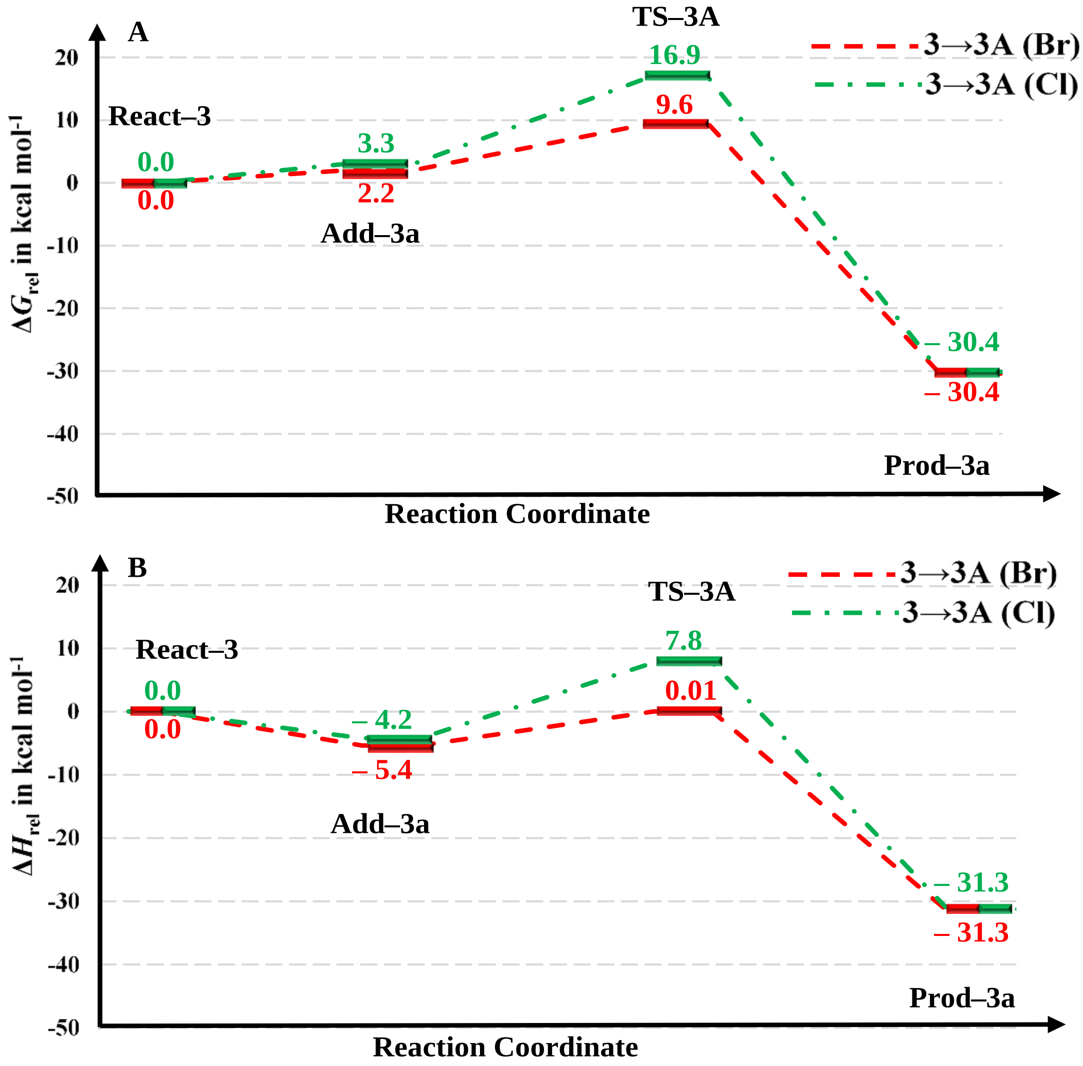


Figure 5.5. The reaction free energy (A) and enthalpy (B) profiles for the reaction **React–3** + 2–X–thiophene → **Prod–3a** at 195.15K**.** Refer to Figure 5.6 and Table 5.2 regarding structures.

carbons. From the reaction profile relating to reaction (***ii***), see Figure 5.5, it is observed that for either halogen the relative free energies calculated for the transition state **TS–3A** are marginally larger than **TS–1A**, by 1.7 and 1.1 kcal mol^{-1} for chlorine and bromine, respectively. The reverse is observed for the relative activation enthalpy, whereby activation is equal to 7.8 kcal mol^{-1} compared to 7.9 kcal mol^{-1} for chlorine and 0.01 compared to 0.2 kcal mol^{-1} for bromine. When observing the transition states **TS–3A**, Figure 5.6, similar TS behaviour is found to that of **TS–1A**, such as the interaction between the chlorine and lithium inducing stability, the less profound Br—Li dispersion interactions and bond stretching exhibited by the C(1)—X and C(2)—Li interactions. So far, the reactions (***i***) *and* (***ii***) are analogous in terms of the transition states formed.

The similarities continue for the heterodimer products **Prod–1a** and **Prod–3a** shown in Table 5.2, where both products favour a dimer arrangement, even so, when explicit THF is present. From the reaction profiles, product **1a** has a relative reaction free energy and enthalpy equal to –31.4 and –31.1 kcal mol^{-1} which is comparable to –30.4 and –31.3 kcal mol^{-1} for products **3a**, respectively.

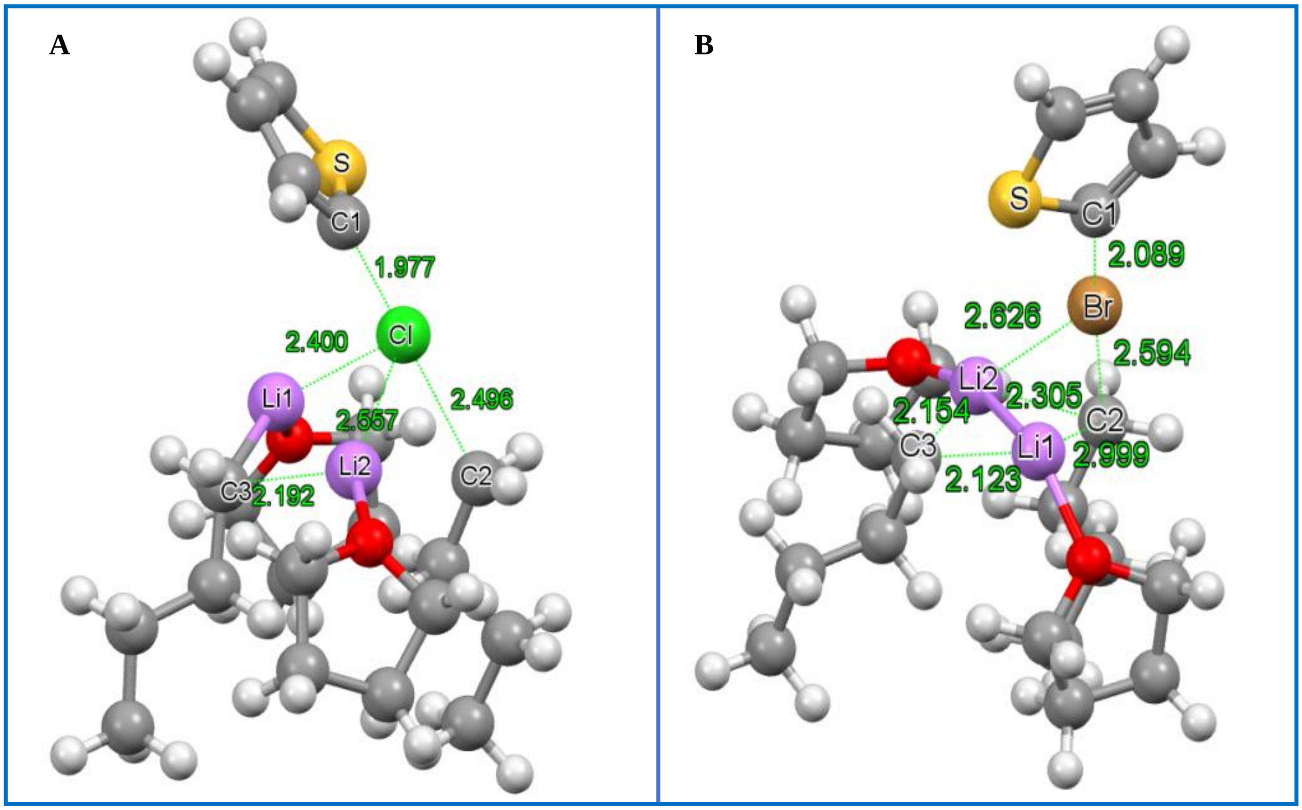
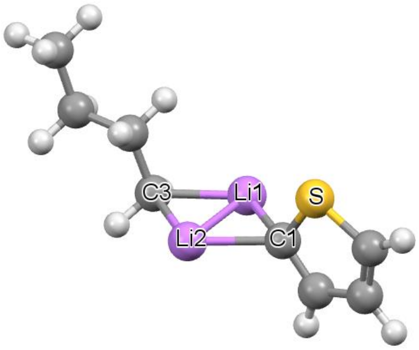
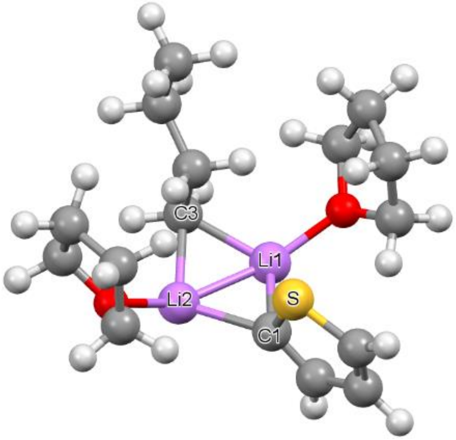


Figure 5.6. Optimised transition structures **TS–3A** for the reactions: **React–3** + 2-Cl-thiophene → **Prod–3a** (A) and **React–3** + 2-Br-thiophene → **Prod–3a** (B). Refer to the reaction energy profiles found in Figure 5.5.

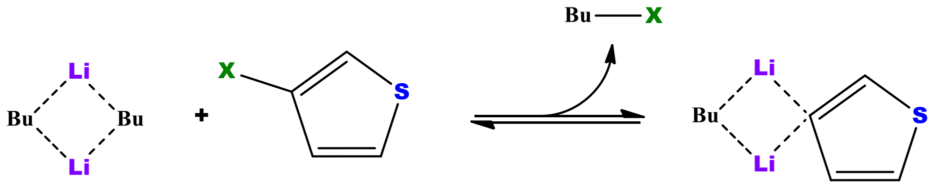
Table 5.2. Relative energies (in kcal mol^{-1}) and computed bond lengths (in Å) for the heterodimers **Prod–1a** and **Prod–3a**.*

	Structures	
	Prod–1a	**Prod–3a**
		
	Rel. Energies	
ΔG_{rel}	–31.4	–30.4
ΔH_{rel}	–31.1	–31.3
Bond	Bond Length	
C(1)—S	1.7660	1.7692
C(1)—C(β)	1.3883	1.3878
C(1)—Li(1)	2.2000	2.2345
C(1)—Li(2)	2.2001	2.1920
C(3)– –C(1)	3.6840	3.5920
Li(1)– –Li(2)	2.3380	2.3708
C(3)—Li(1)	2.1644	2.1417
C(3)—Li(2)	2.1643	2.1763

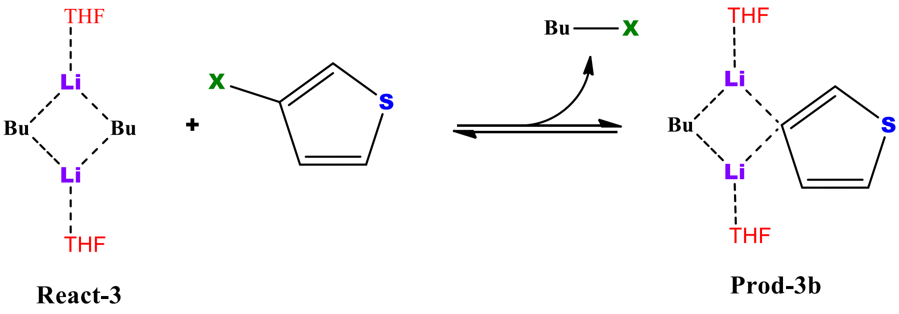
*Refer to the reaction energy profiles found in Figures 5.3 and 5.5.

5.4.4. Reaction energy profiles: 1st step in beta lithium-halogen exchange reactions

Moving on to the first beta step reaction, reactions ***(iii)*** and ***(iv)*** involve reacting *n*-BuLi reactant species **React–1** and **React–3** with a mono β-halogenated thiophene:



React-1 **Prod-1b** ***(iii)***



(*iv*)

Regarding the adducts **Add–1b** and **Add–3b** for reactions **(*iii*)** and **(*iv*)** (Figures 5.7 and 5.8), respectively, the relative free energies infer that the structures are moderately unfavourable, while the relative enthalpies infer that the reaction is exothermic and stable. Before looking further at the reaction energy profiles and it should be reiterated that a halogen located at the β-position on the thiophene ring is considered the more stable reactant, and literature states that the β-position is an order of magnitude less acidic compared to the α-position.[16] Therefore, when considering the TSs,

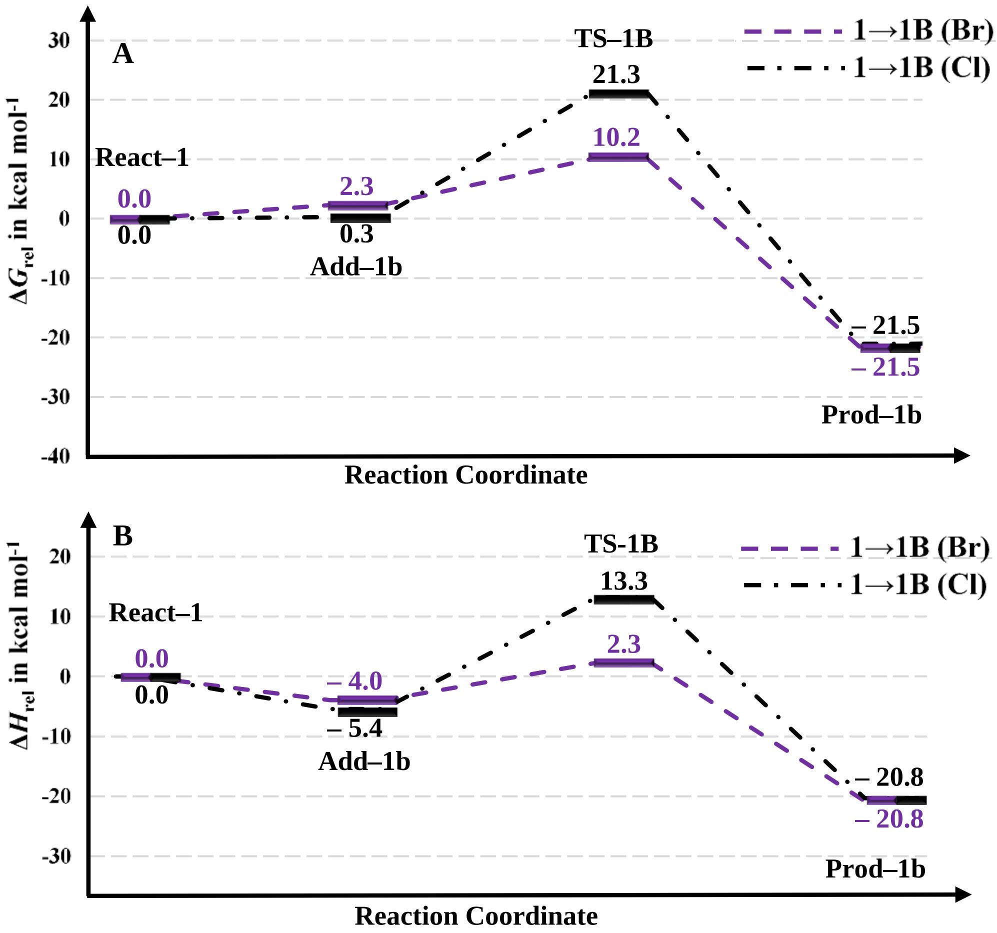


Figure 5.7. The reaction free energy (A) and enthalpy (B) profiles for the reaction **React–1** + 3–X–thiophene → **Prod–1b** at 195.15K**,** implementing CSM. Refer to Figure 5.9 and Table 5.3 regarding structures.

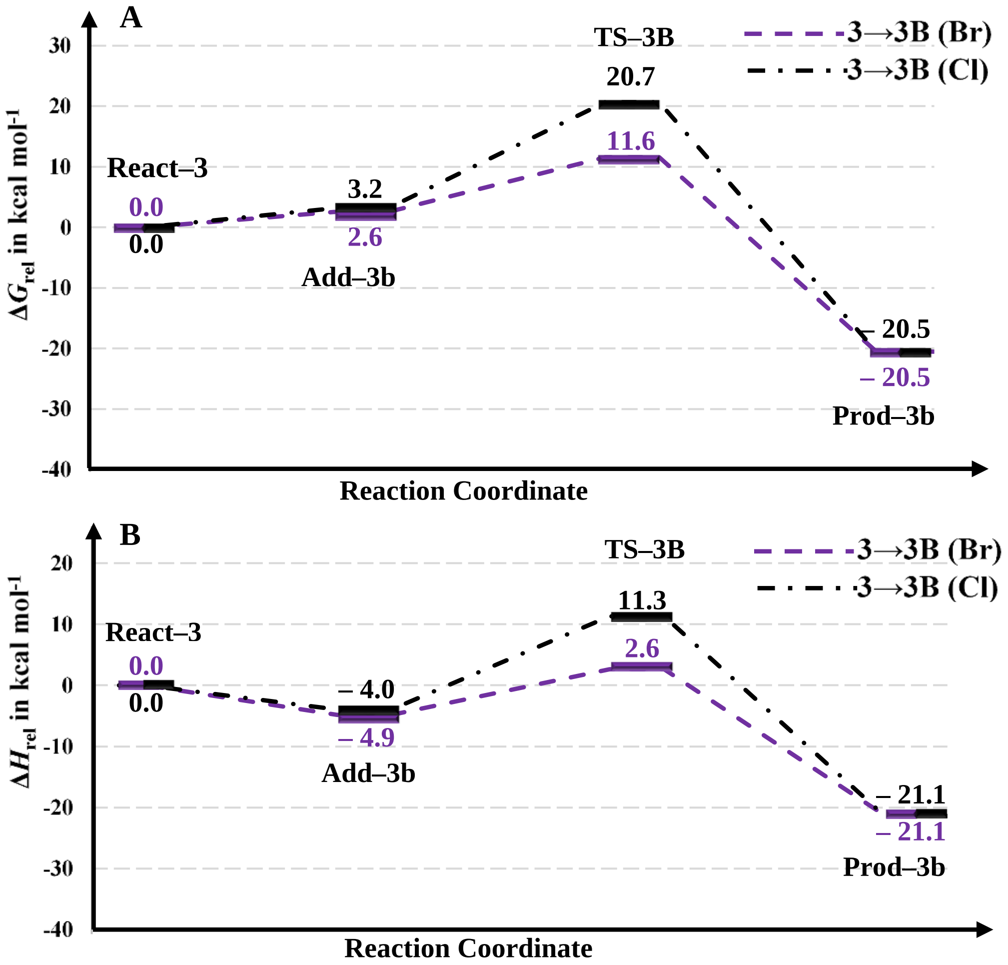


Figure 5.8. The reaction free energy (A) and enthalpy (B) profiles for the reaction **React–3** + 3–X–thiophene → **Prod–3b** at 195.15K**,** implementing a HSM. Refer to Figure 5.9 and Table 5.3 regarding structures.

it is expected that the activation barriers for **TS–1B** and **TS–3B** are to be greater in comparison to **TS–1A** and **TS–3A**, respectively. For each stationary point **TS–1B** and **TS–3B** the activation free energy barriers are ca. 10.2, 11.6 kcal mol^{-1} and 21.3, 20.7 kcal mol^{-1}, respectively for bromine and chlorine. Similarly, for activation enthalpies, it is observed that chlorine exhibits a larger activation barrier (13.3 & 11.3 kcal mol^{-1}) in comparison to bromine (2.3 & 2.6 kcal mol^{-1}). Once again, it is observed that the bromine species generate a stationary point (TS) which is lower in energy along the reaction profile compared to chlorine. This is evident from the transition states **TS–1A** and **TS–3A**, which have favoured stability over **TS–1B** and **TS–3B** whereby the difference in relative energies ranges from 1.5 up to 6.0 kcal mol^{-1}. Therefore, it is apparent that when performing lithium-halogen exchange on the thiophene ring, the α-position is preferred.

Comparison of the structural environment of the transition states found in Figure 5.9, all the β–halogen systems resemble one another by forming the prominent ate-complex. The ate-complex is generally illustrated to include one Li^+ ion to counter the (*n*-BuLi–X–*n*-BuLi)$^-$ negative charge,[5] but for **TS–1B** and **TS–3B** this is not the case. Both lithium atoms seem to be positioned at a relatively equal distance from the halogen, suggesting a di-lithium complex interaction with the halogen. In addition, this behaviour is also observed for both **TS–3A** structures and the bromine **TS–1A** system. Furthermore, there is noticeable bond stretching between the C(2)—X and C(3)—Li bonding interactions.

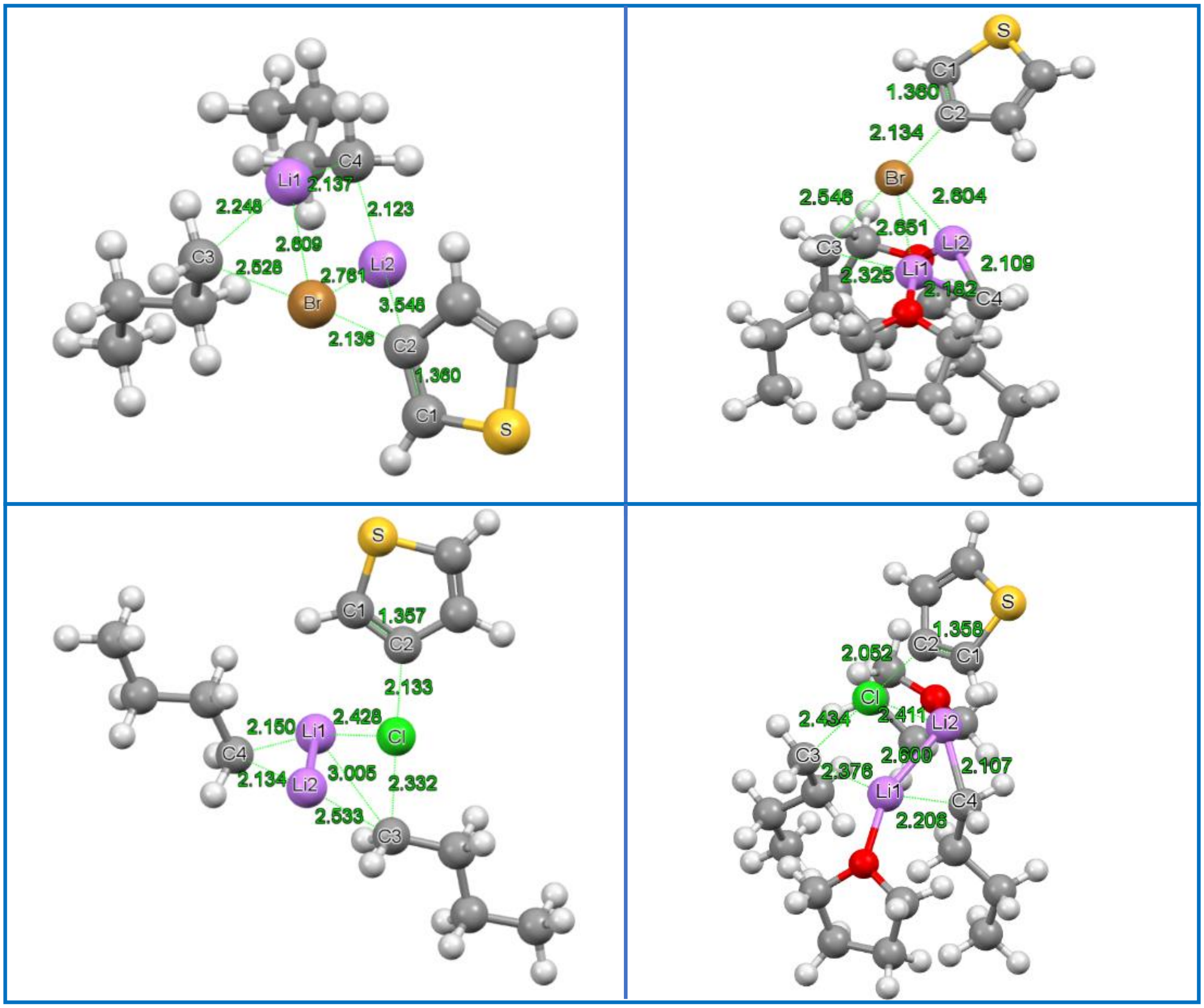
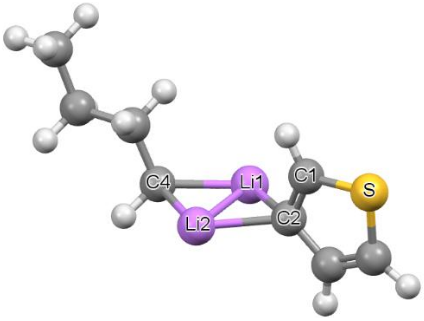
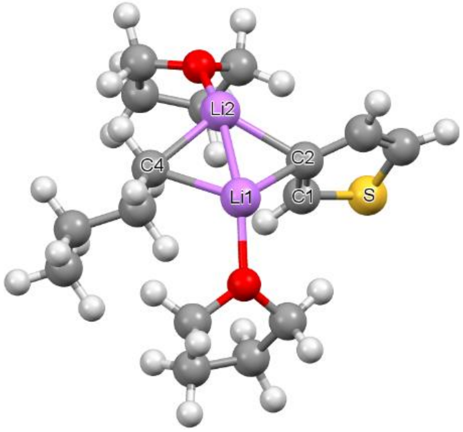


Figure 5.9. Optimised transition structures **TS–1B** and **TS–3B** for the reactions: **React–1** + 3-Br-thiophene → **Prod–1b** (A), **React–1** + 3-Cl-thiophene → **Prod–1b** (B), **React–3** + 3-Br-thiophene → **Prod–3b** (C) and **React–3** + 3-Cl-thiophene → **Prod–3b** (D). Refer to the reaction energy profiles found in Figures 5.7 and 5.8.

Next to be discussed is that of products **Prod–1B** and **Prod–3B,** which are minima on the reaction profiles, see Table 5.3. Product **1B** has a relative free energy and reaction enthalpy of –21.5 and –20.8 kcal mol^{-1}, respectively. This is comparable to –20.5 and –21.0 kcal mol^{-1} for product **3B**. When comparing the stability of products **1B** and **3B** with that of **1A** and **3A**, respectively, it is undeniable that the latter alpha products are more stable by c.a 10 kcal mol^{-1}. Therefore, the thiophene ring shows favourable stability at the β-position over the α-position when substituted by an electron withdrawing group (e.g. 3-bromothiophene), but the reverse is observed when an electron donating group (i.e. lithium) lies at the β-position.

Table 5.3. Relative energies (in kcal mol^{-1}) and computed bond lengths (in Å) for the heterodimers **Prod–1b** and **Prod–3b**.*

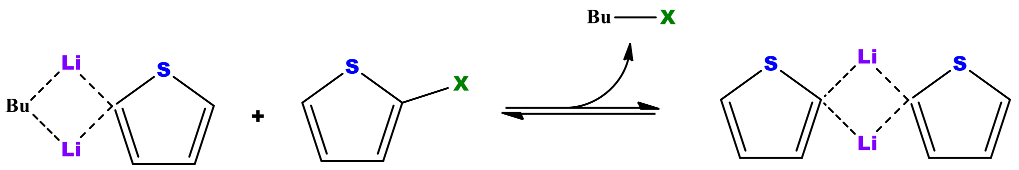
	Structures	
	Prod–1b	**Prod–3b**
		
	Rel. Energies	
ΔG_{rel}	–21.5	–20.5
ΔH_{rel}	–20.8	–21.1
Bond	Bond Length	
C(1)—S	1.7720	1.7722
C(1)—C(2)	1.3745	1.3728
C(2)—Li(1)	2.1941	2.1944
C(2)—Li(2)	2.1935	2.2001
C(2)– –C(4)	3.6864	3.5853
Li(1)– –Li(2)	2.3250	2.3512
C(4)—Li(1)	2.1708	2.1811
C(4)—Li(2)	2.1709	2.1566

*Refer to the reaction energy profiles found in Figures 5.7 and 5.8.

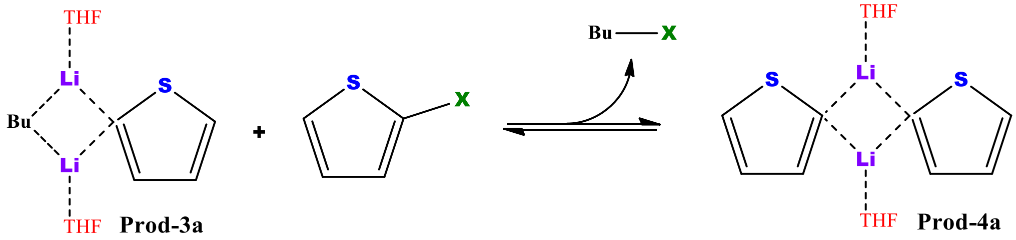
Lastly, the products generated by implementing either a CSM (**1A** and **1B)** or a HSM (3**A** and **3B)** are analogous in terms of structure and bond parameters. The only significant variations observed is that of the Li(1)– –Li(2) and C(2)– –C(4) spatial distance. Structurally the di-solvated dimer has electron withdrawing oxygen bonded to each lithium, therefore the Li– –Li spatial displacement is slightly increased, which decreases the C(2)– –C(4) spatial distance to counteract the former geometry change.

5.4.5. Reaction energy profiles: 2nd alpha lithium-halogen exchange reactions.

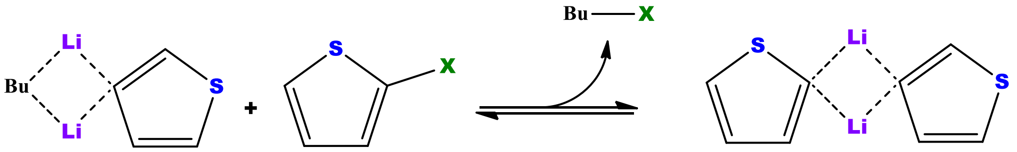
The organolithium stationary points **Prod–1a**, **Prod–3a**, **Prod–1b** and **Prod–3b** are heterodimers made of one lithiated thiophene and *n*-BuLi. Usually, when conducting an experimental procedure, the mole ratio for each involved reactant would be at least 1:1. Therefore, the products **Prod–1a**, **Prod–3a**, **Prod–1b** and **Prod–3b** should undergo an additional lithium-halogen exchange reaction with any remaining 2–X–thiophene. Hence, the following reactions were computed:



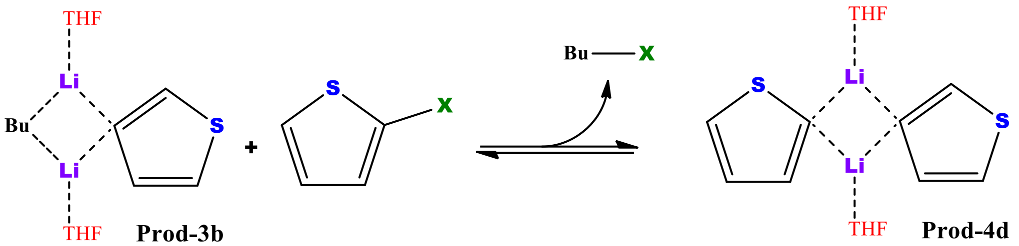
Prod-1a **Prod-2a** **(*v*)**



Prod-3a **Prod-4a** **(*vi*)**



Prod-1b **Prod-2d** **(*vii*)**



Prod-3b **Prod-4d** **(*viii*)**

Of the four alpha reactions, only reactions (***v***) and (***vi***) will be discussed here in detail. Please refer to the Supporting Information, Appendix C for reaction data and structures pertaining to the exchange reactions (***vii***) and (***viii***).

Modelling using the Continuous Solvation Model

The energy reaction profiles regarding the CSM reaction (***v***) can be found in Figure 5.10 where a recurrent reaction profile is observed for the alpha exchange. Before the formation of the product **Prod–2a**, the reaction undergoes two physical changes to generate the stationary point. The first stationary point is that of the adduct **Add–2a**, where the adduct formation is favourable in terms of relative enthalpies but unstable with regards to the relative free energies. Therefore, the overall formation behaviour is both exothermic and non-favourable (non-spontaneous).

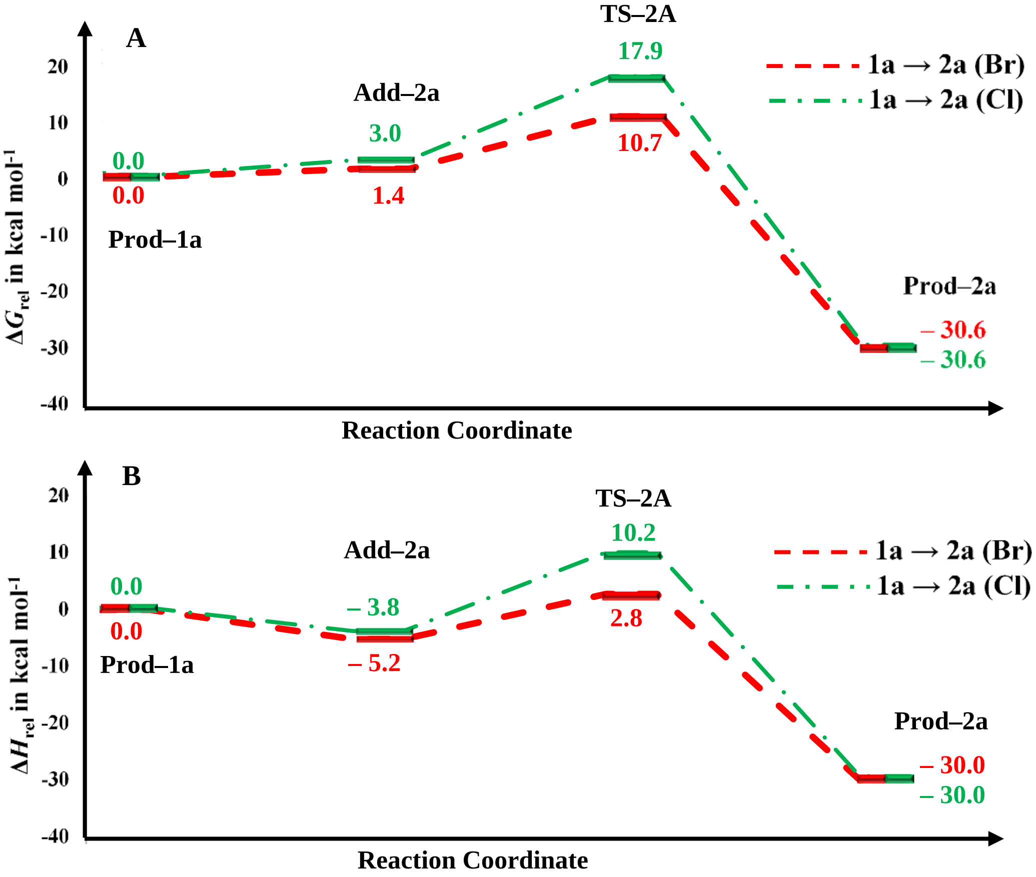


Figure 5.10. The reaction free energy (A) and enthalpy (B) profiles for the reaction **Prod-1a** + 2–X–thiophene → **Prod–2a** at 195.15K**,** implementing a CSM. Refer to Figure 5.11 and Table 5.4 regarding structures.

The next stationary point of interest is that of the transitions states, which are very important in helping to define the reaction mechanism for the second alpha exchange. The TS associated with bromine forms the more favourable stationary point. The energy difference is ca. 7 kcal mol^{-1} in favour of bromine compared to chlorine. With the noticeable difference, there should be an observed difference in the structural TSs parameters to explain bromines preferred stability over chlorine. An overview of the TS structures, Figure 5.11, indicates that the ate–complex formation is present for each TS where the two lithiums are interacting with the halogen, providing possible stability to the anionic reactive moiety; (Thio-C(3)–X–C(5)-Thio)$^{-}$. Furthermore, the only noticeable differences are that of the X—Li and X—C(5) bonding interactions, where for Br—Li and Cl—Li, the average interacting distance are 2.565 and 2.468 Å, respectively. Similar behaviour is observed for the Br—C(5) and Cl—C(5), where the bond distance is 2.159 and 2.010 Å, respectively. Overall, chlorine has shorter bond length interactions compared to that of the larger bromine. Possible explanations as to why the chlorine TS species generate a larger activation barrier is the lability of the halogen and α-carbon C(5) bond, which is dependent on the electronegativity and size of the anionic-halogen. When observing the mono-halogenated reactants in Figure 5.2, it is observed that the chlorine to α-carbon bond distance is ca. 0.1 Å shorter than that of the bromine to α-carbon bond. If relating to electronegativity and size, bromine can facilitate a negative electron more readily (localised) thus, forming an activation barrier (TSs) that is lower in energy compared to chlorine. In conclusion, the more electron delocalised chlorine bond requires additional energy to cleave and is intrinsically less capable to stabilise a negative charge, resulting in an increased activation energy barrier.

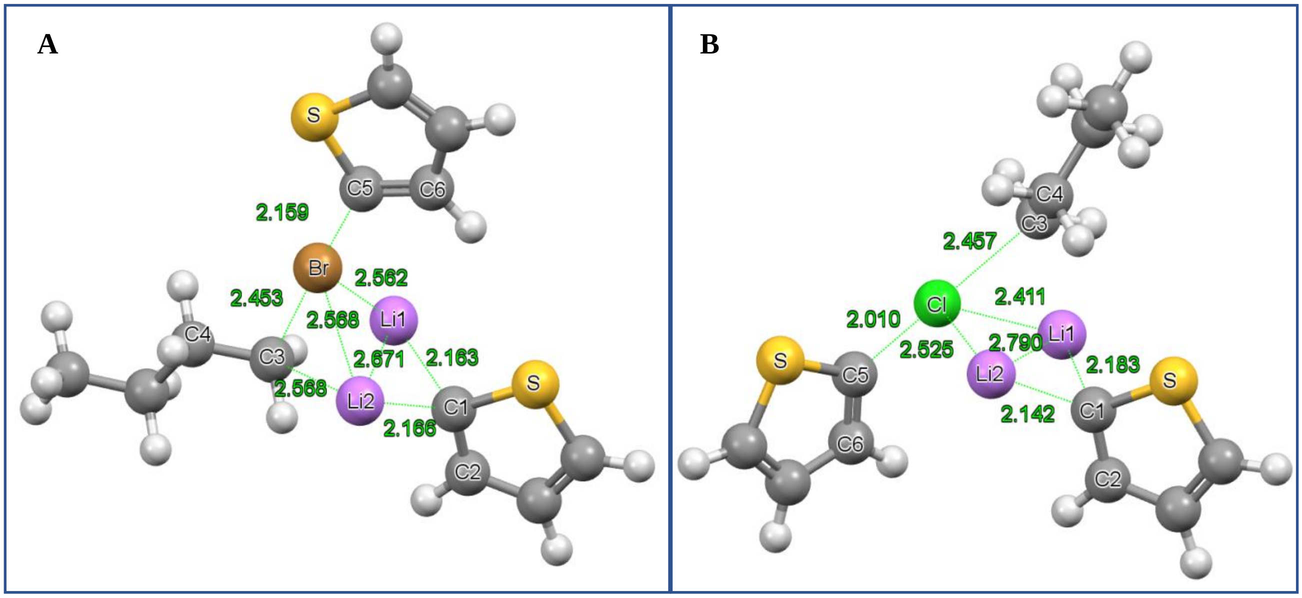


Figure 5.11. Optimised transition structures **TS–2A** for the reactions: **Prod–1a** + 2-Br-thiophene → **Prod–2a** (A) and **Prod–1a** + 2-Cl-thiophene → **Prod–2a** (B). Refer to the reaction energy profiles found in Figure 5.10.

Modelling using the hybrid solvation model

The energy reaction profiles regarding the HSM reaction (***vi***) can be found in Figure 5.12. From the exothermic and slightly unstable adducts to the bromine exchange TS having significant favourability over the chlorine, the reaction profile is analogue to that of the CSM exchange reaction profile, Figure 5.10. Although similar, it is noticeable that the presence of explicit THF has lowered the relative activation free energy by c.a. 2 and 3 kcal mol^{-1} for bromine and chlorine, respectively. The relative activation enthalpy is c.a. 2 kcal mol^{-1} more favoured for both halogens and their TSs. So, for the second step alpha exchange reaction it is observed that the HSM exhibits a lowering in activation energy than that of the CSM, while for the first step alpha exchange reactions energy profiles the reverse is observed, see Figures 5.3 and 5.5.

Looking at the TS structures **TS–4A** found in Figure 5.13, an ate-complex is formed. Comparing the structures to that of the CSM, it is observed that the X—C(5) bond length is shorter for both TSs,

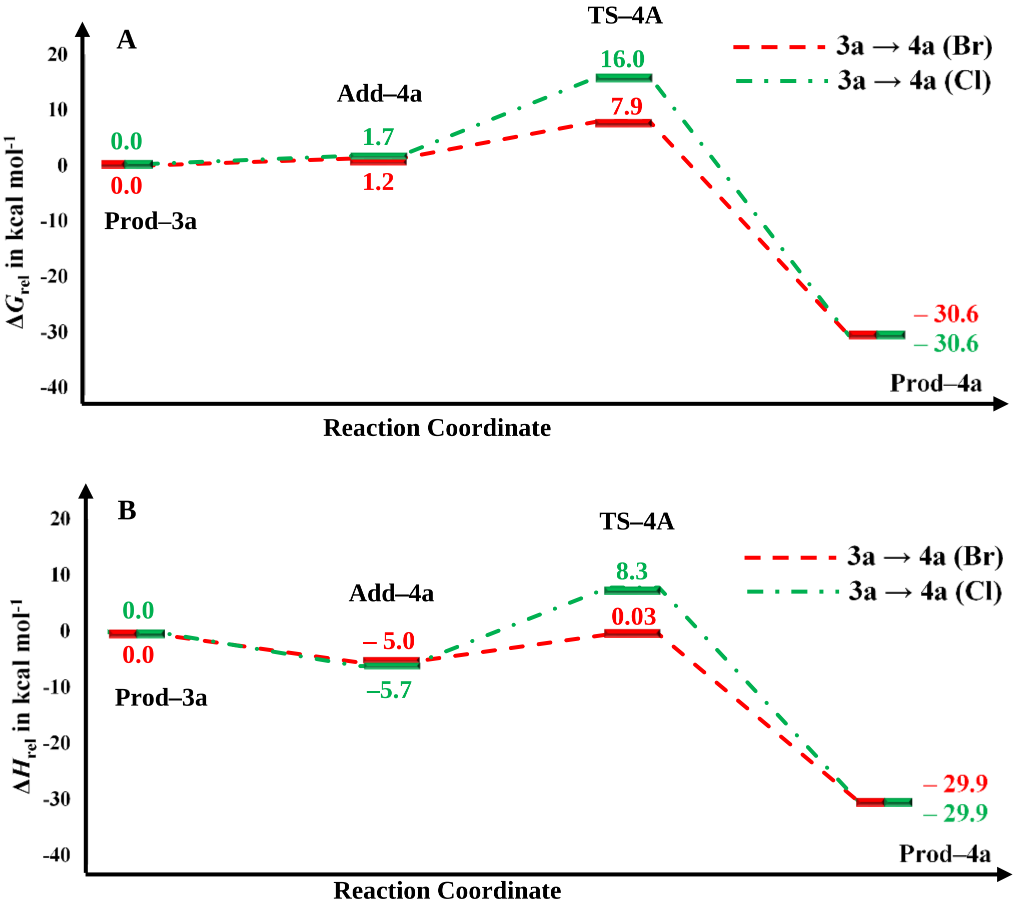


Figure 5.12. The reaction free energy (A) and enthalpy (B) profiles for the reaction **Prod-3a** + 2–X–thiophene → **Prod–4a** at 195.15K**,** implementing a HSM. Refer to Figure 5.13 and Table 5.4 regarding structures.

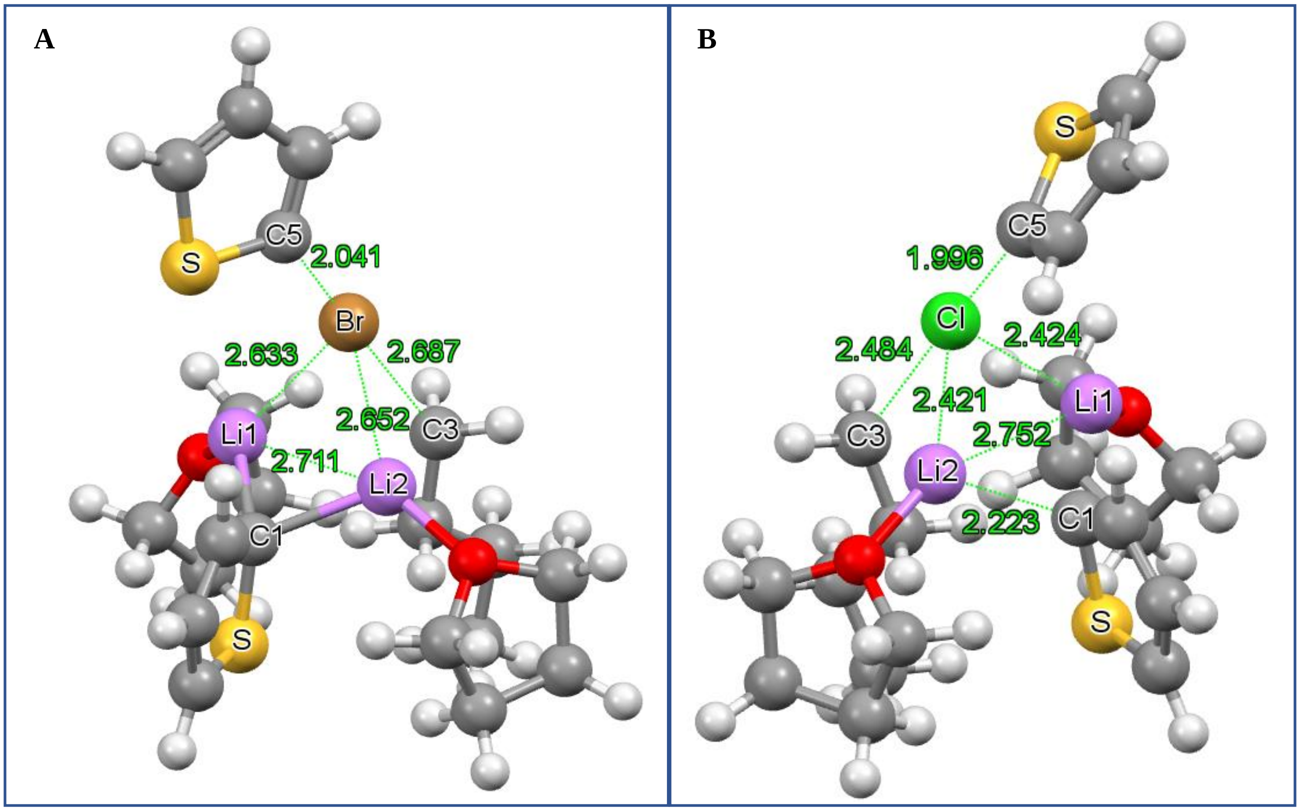
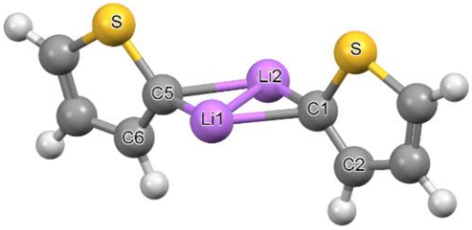
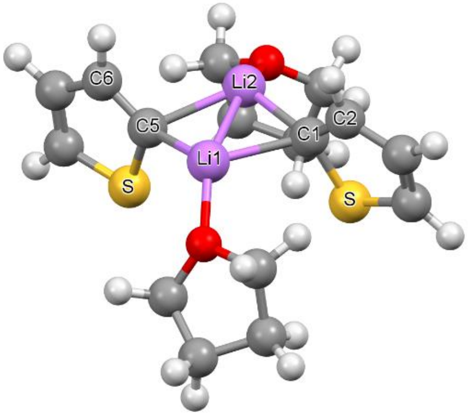


Figure 5.13. Optimised transition structures **TS–4A** for the reactions: **Prod–3a** + 2-Br-thiophene → **Prod–4a** (A) and **Prod–3a** + 2-Cl-thiophene → **Prod–4a** (B). Refer to the reaction energy profiles found in Figure 5.12.

hence, a larger X—C(3) bond length. This would suggest that the presence of explicit THF stabilises the system allowing the exchange reaction to occur more readily while the halogen approaches the butyl α–carbon, C(3). The average Br—Li bond length is 2.643 Å which is c.a. 1 kcal mol^{-1} larger than that of **TS–2A**, while for the chlorine system the average Cl—Li bond is unchanged between the two solvation models.

Next is the comparison of the computed 2–lithiothiophene homodimer products **Prod–2a** and **Prod–4a** shown in Table 5.4. Each homodimer favours the dimer arrangement, even so, when explicit THF is present. This aggregate formation is equivalent to that of the alpha–heterodimers found in Table 5.2. Product **2a** has a relative reaction free energy and enthalpy equal to –30.6 and –30.0 $kcal.mol^{-1}$ which corresponds to –30.6 and –29.9 $kcal.mol^{-1}$ for product **4a**, respectively. Lastly, the structures shown in Table 5.4 are the homodimers exhibiting the cis stereochemistry, this is to state that the cis orientation is preferred over the trans. The difference between the two stereochemistry's is less than 1 kcal mol^{-1}, which would imply that either product should be present in solution, despite literature stating that the homodimer exists as a mixture between monomer and dimer in THF solution. [3]

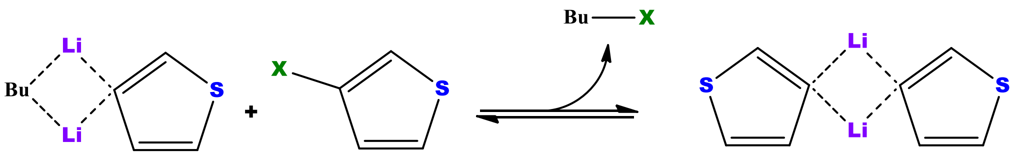
Table 5.4. Relative energies (in kcal mol^{-1}) and computed bond lengths (in Å) for the heterodimers **Prod–2a** and **Prod–4a**.*

	Structures	
	Prod–2a	**Prod–4a**
		
	Rel. Energies	
ΔG_{rel}	–30.6	–30.6
ΔH_{rel}	–30.0	–29.9
Bond	Bond Length	
C(1)—S	1.7659	1.7682
C(1)—Li(1)	2.2076	2.2344
C(1)—Li(2)	2.1673	2.1601
C(1)– –C(5)	3.6240	3.6027
Li(1)– –Li(2)	2.4495	2.4624
C(5)—S	1.7659	1.7671
C(5)—Li(1)	2.1678	2.1592
C(5)—Li(2)	2.2065	2.2257

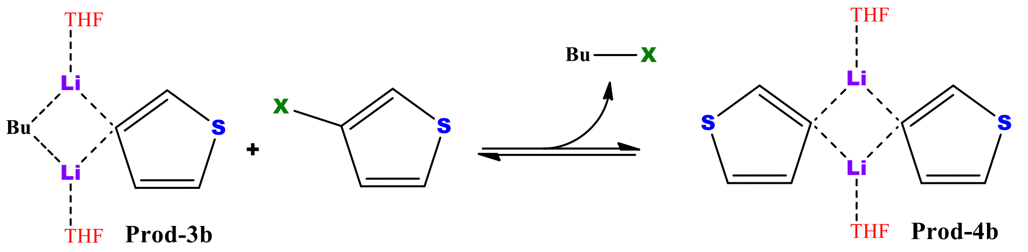
*Refer to the reaction energy profiles found in Figures 5.10 and 5.12.

5.4.6. Reaction energy profiles: 2$^{\mathrm{nd}}$ beta lithium-halogen exchange reactions

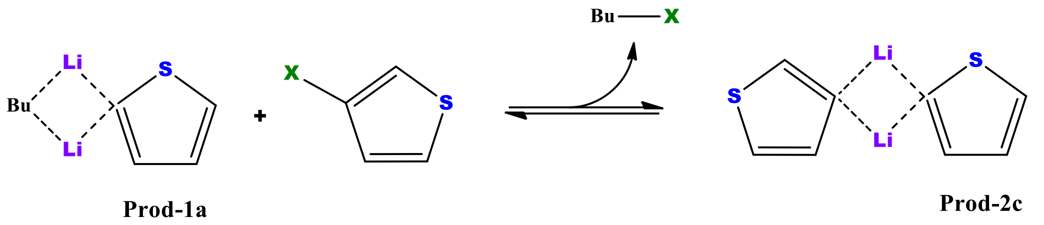
Like with the second alpha step, the organolithium stationary points **Prod–1b**, **Prod–3b**, **Prod–1a** and **Prod–3a** can undergo an additional lithium-halogen exchange reaction with any present or remaining mono β-halogenated thiophene. Hence, the following reactions were computed:



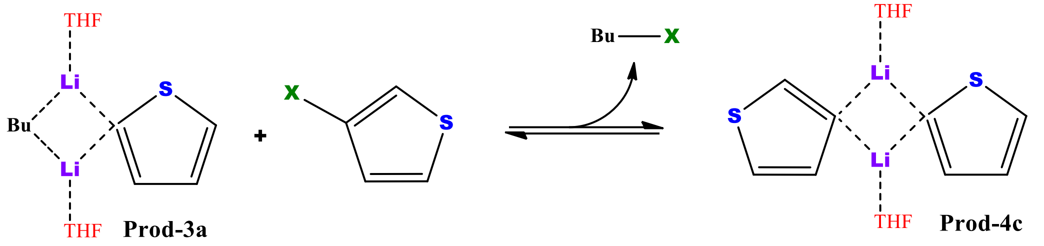
Prod-1b **Prod-2b** (*ix*)



(***x***)



(***xi***)



(***xii***)

Of the four beta reactions, only reactions (***ix***) and (***x***) will be discussed here in detail. Please refer to the Supporting Information, Appendix C for reaction data pertaining to the exchange reactions (***xi***) and (***xii***).

Before looking at the reaction energy profiles pertaining to reactions (***ix*)** and (***xi*)**, Figures 5.14 and 5.15, respectively, it should be reiterated that the beta substituted products **Prod–1b** and **Prod–3b** are less stable than the alpha-substituted heterodimers **Prod–1a** and **Prod–3a**. Therefore, when considering the transition states, it is expected that the activation energy barriers for **TS–2B** and **TS–4B** are to be greater in comparison to **TS–2A** and **TS–4A**, respectively. From the reaction profiles regarding stationary point **TS–2B** and **TS–4B** the relative activation free energy barriers are ca. 9.8, 8.4 kcal mol^{-1} and 19.3, 17.3 kcal mol^{-1}, respectively for bromine and chlorine. Similarly, for activation enthalpies, it is observed that chlorine exhibits a larger activation energy barrier (11.0 & 9.5 kcal mol^{-1}) in comparison to bromine (1.9 & 0.2 kcal mol^{-1}). When comparing the relative energy values to that of the first beta step exchange reaction it was observed that the TS activation energy barriers computed with either solvation model were equivalent in the case of bromine. For chlorine though, it was observed that the HSM generated an activation energy barrier

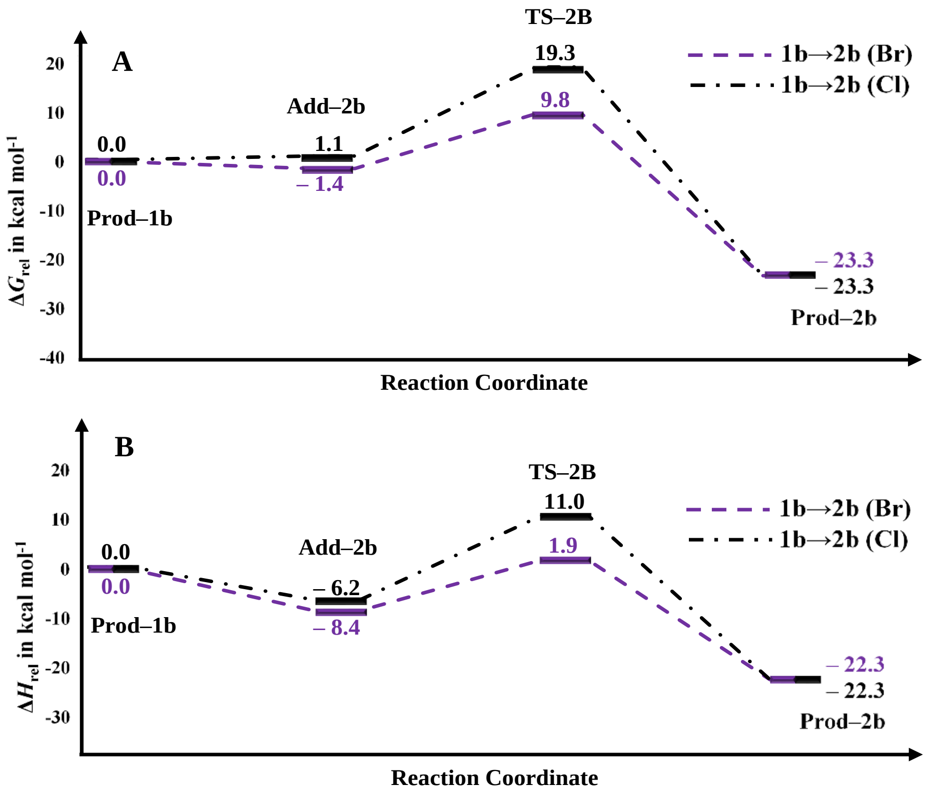


Figure 5.14. The reaction free energy (A) and enthalpy (B) profiles for the reaction **Prod-1b** + 3–X–thiophene → **Prod–2b** at 195.15K, implementing a CSM. Refer to Figure 5.16 and Table 5.5 regarding structures.

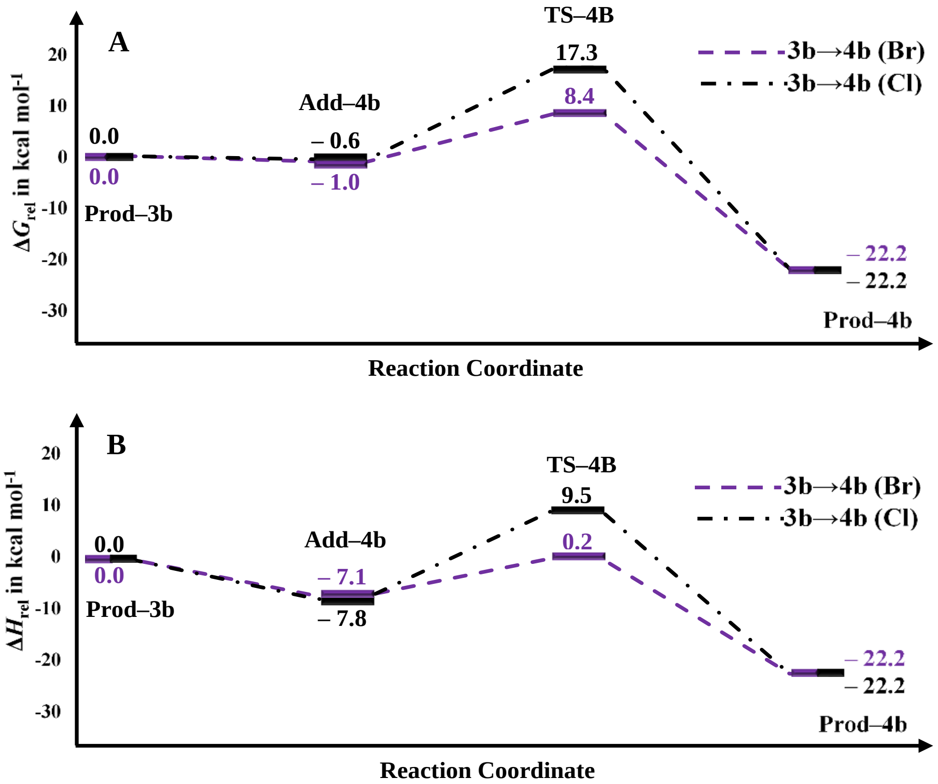


Figure 5.15. The reaction free energy (A) and enthalpy (B) profiles for the reaction **Prod-3b** + 3–X–thiophene → **Prod–4b** at 195.15K, implementing a HSM. Refer to Figure 5.16 and Table 5.5 regarding structures.

that was 1.4 kcal mol^{-1} larger than that of CSM. Whereas now each activation energy barrier computed has the HSM forming the more favourable TSs by up to 2 kcal mol^{-1}. This computed behaviour was also observed for the second alpha exchange reactions.

Looking at the transition state structures found in Figure 5.16, one can conclude that the β–halogen systems resemble one another by forming the prominent ate-complex. Compared to chlorine, bromines TS structures have on average larger bond lengths between the halogen and all interacting carbon and lithium atoms. Furthermore, the TS generated with the HSM has increased stability due to the explicit THF, which have allowed the system to undergo exchange reaction while the halogen is situated slightly further from the butyl α–carbon, as opposed to the CSM, computed TSs.

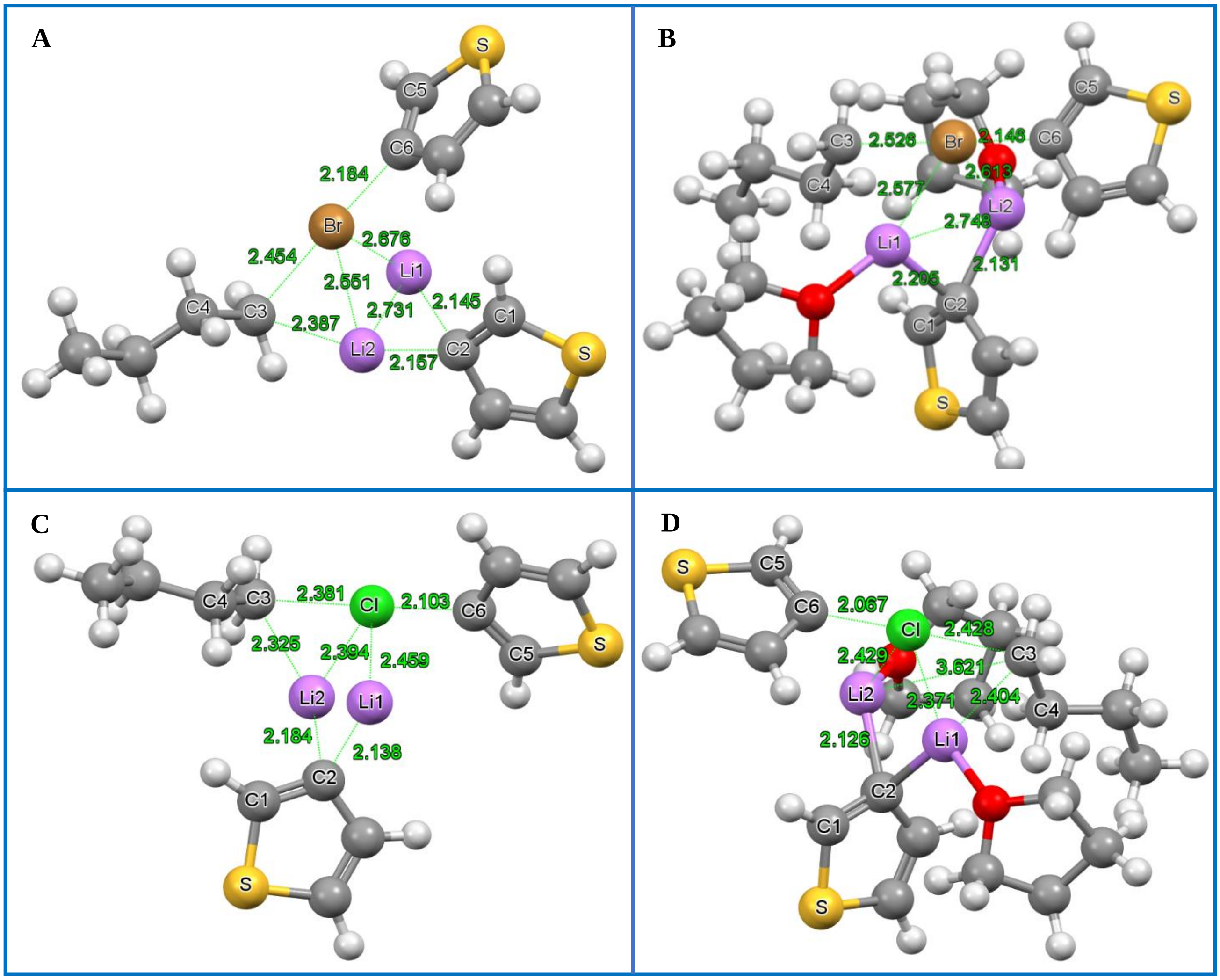
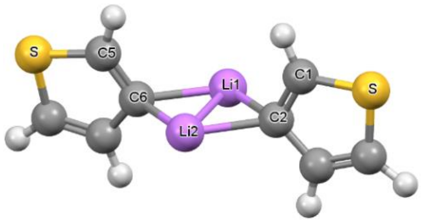
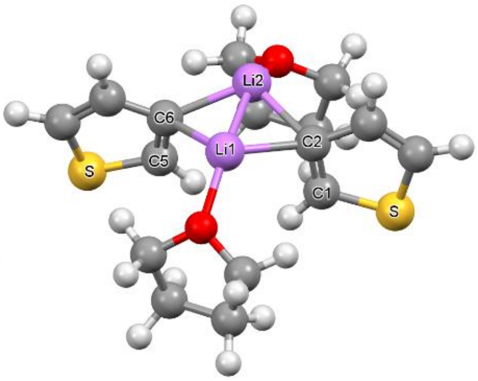


Figure 5.16. Optimised transition structures **TS–2B** and **TS–4B** for the reactions: **Prod–1b+** 3-Br-thiophene → **Prod–2b** (A), **Prod–2b +** 3-Br-thiophene → **Prod–4b** (B), **Prod–1b +** 3-Cl-thiophene → **Prod–2b** (C) and **Prod–2b +** 3-Cl-thiophene → **Prod–4b** (D). Refer to the reaction energy profiles found in Figures 5.14 and 5.15.

Lastly, the comparison of the computed 3–lithiothiophene homodimer products **Prod–2b** and **Prod–4b** are shown in Table 5.5. Each homodimer favours the dimer arrangement, even so, when explicit THF. Product **2b** has a relative reaction free energy equal to –23.3 kcal.mol^{-1} which is 1.1 kcal mol^{-1} more stable than that of product **4b**. The reaction enthalpies, on the other hand, are equivalent between the two products. Based on their relative energies it is found that the beta homodimer products are the least stable products when compared to the alpha homodimers products **Prod–2a** and **Prod–4a**, see Table 5.4. Each product can either adopt a cis or trans stereochemistry and for **Prod–2b** and **Prod–4b** the former is favoured, which correlates with **Prod–2a** and **Prod–4a**. Although there is a preference in the isomer stereochemistry, the difference in energies between cis and trans isomers is less than ca. 1 kcal.mol^{-1}. Refer to the Supporting Information, Appendix C.

Table 5.5. Relative energies (in kcal mol^{-1}) and computed bond lengths (in Å) for the heterodimers **Prod–2b** and **Prod–4b**.*

	Structures	
	Prod–2b	**Prod–4b**
		
	Rel. Energies	
ΔG_{rel}	–23.3	–22.2
ΔH_{rel}	–22.3	–22.2
Bond	Bond Length	
C(α)—S[a]	1.7707	1.7702
C(α)—C(β)[a]	1.3747	1.3734
C(2)—Li(1)	2.1932	2.1690
C(2)—Li(2)	2.1690	2.2037
C(2)– –C(6)	3.6430	3.5462
Li(1)– –Li(2)	2.4013	2.4153
C(6)—Li(1)	2.1689	2.2037
C(6)—Li(2)	2.1957	2.1689

[a] The average bond lengths are reported

*Refer to the reaction energy profiles found in Figures 5.14 and 5.15.

5.4.7. Summary: Reaction Mechanism

Till now, the results have described the TS stationary point in relation to the stereochemical environment. One important characteristic of a TS is to analyse the single imaginary frequency mode. To serve as an example, only the imaginary frequencies for transitions states **TS–1A** and **TS–4B** will be shown, see Figure 5.17. One of the largest displacement vectors pertaining to the imaginary frequency mode is that of the halogen. The halogen displacement is along the C(1)—X—C(3) bridging for both **TS-1A** and **TS-4B**. As the halogen approaches the butyl C(3) α–carbon, an observed bond dissociation of the lithium atoms with α-carbon C(3) occurs. During the displacement

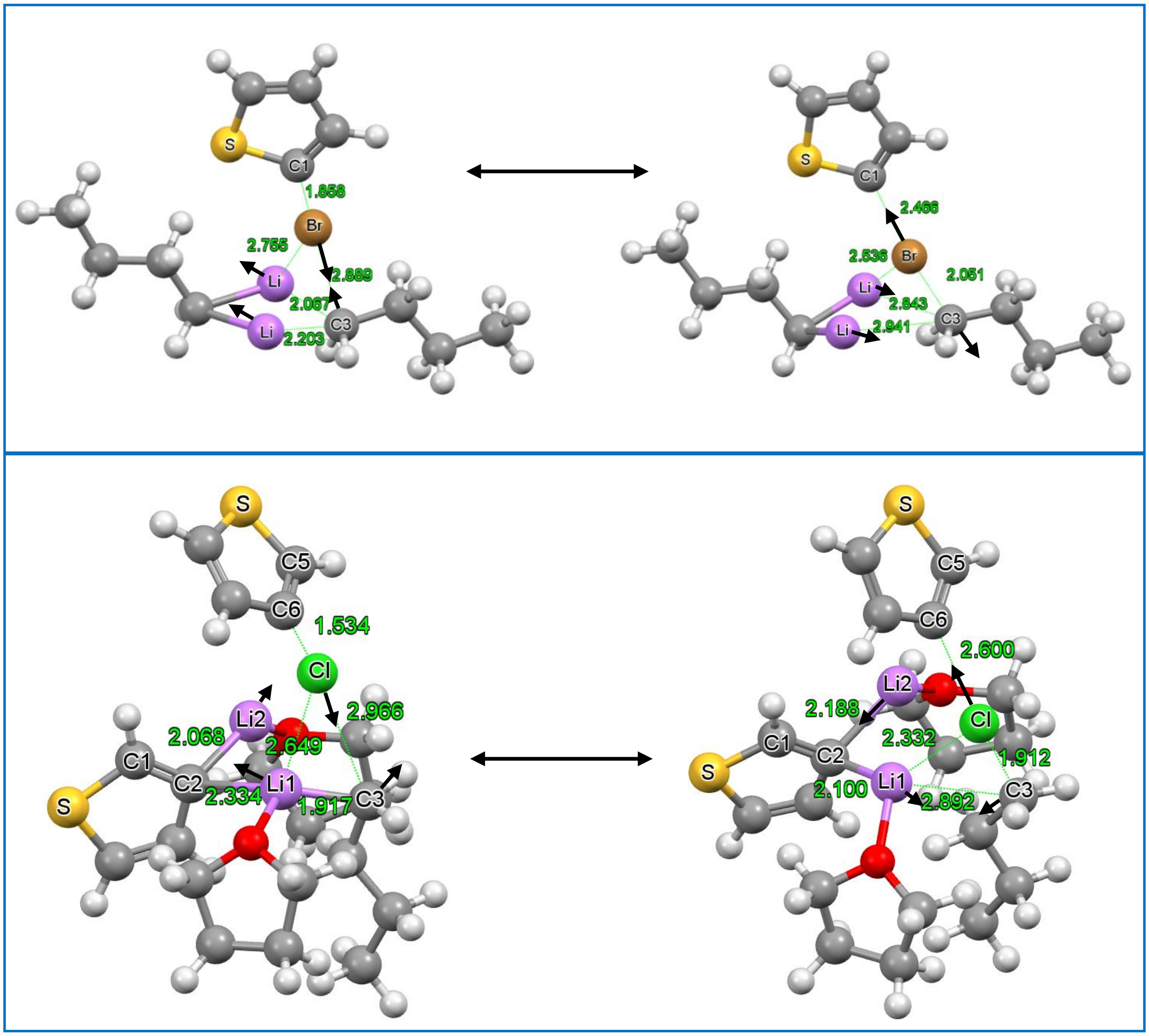


Figure 5.17. The imaginary frequency of the optimised transition structures **TS–1A** (A) & **TS–4B** (B)**,** for the reactions: **1 +** 2-Br-thiophene → **1A** & **3B +** 3-Cl-thiophene → **4B**, computed at195.15 Kelvin. Refer to the reaction energy profiles found in Figures 5.3 and 5.15.

of the halogen towards C(3), the anionic $[C(1)—X—C(3)]^-$ ate-complex is stabilised by the polar attraction of either one or two of the lithium atoms. Please note that bromine generates a TS that is significantly more favoured (lower energy barrier) than that of chlorine, thus suggesting that the intrinsically larger and more electron-rich bromine atom does not require significant interaction with the cationic lithium atoms. Therefore, when modelling transition states for systems undergoing lithium-halogen exchange, the criteria for an acceptable imaginary frequency mode is one that demonstrates the displacement of both the halogen and lithium atoms, forming the reactive ate–complex.

The Overall Complete Reaction Profiles:

The complete overall reaction profiles seen in Figures 5.18 to Figure 5.21 are pertaining to reactions (***i***) through to (***xii***). In each reaction profile, the energies reported are relative to the *n*-BuLi homodimer (solvated or unsolvated). From the reaction profiles reported, it is observed that the reaction is favourable in the forward direction as each homo- and heterodimer product is found to be lower in energy. Of the different alpha and beta-substituted products, the alpha is most favourable. Hence, it is apparent that when performing lithium-halogen exchange on the thiophene ring, the α-position is preferred. Hypothetically, if a reaction mixture contains both alpha– and beta–halogenated thiophene along with a limited quantity of *n*-BuLi, the major product should be that of **Prod–a**, followed by products **Prod–c/d** and the minor product would be **Prod–b**. Although literature states that the lithiated thiophene exists as a mixed aggregate in solution interconverting between dimer and monomer, the preferred and most stable oligomer is that of the dimer. The reason being that each reaction modelled ended up with the dimer intact and no monomer product species generated.

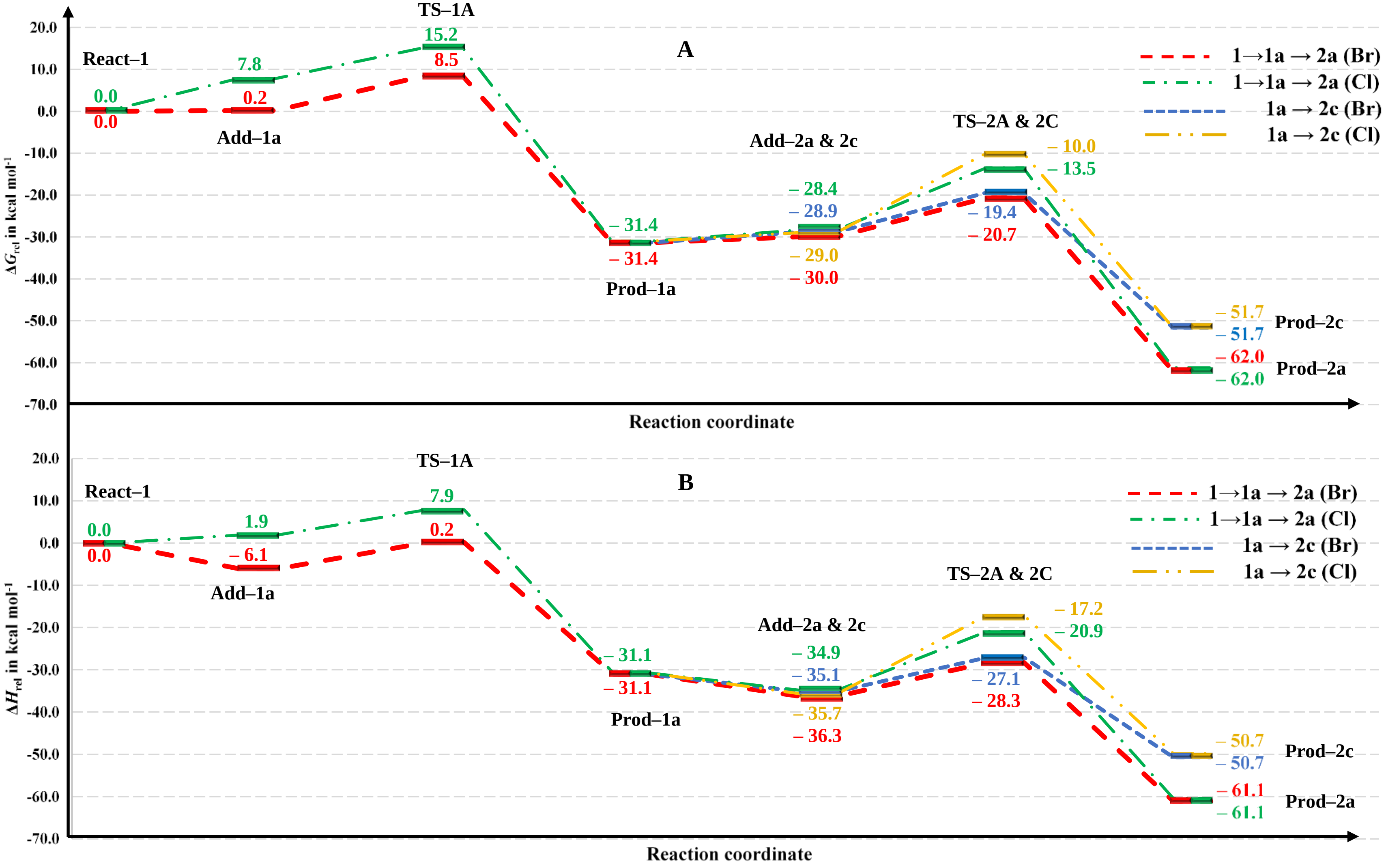


Figure 5.18. The complete overall reaction free energy (A) and enthalpy (B) profiles for the reactions of: **React–1** + 2–X–thiophene → **Prod–1a, Prod–1a** + 2–X–thiophene → **Prod–2a** and **Prod–1a** + 3–X–thiophene → **Prod–2c** at 195.15K**,** implementing a CSM.

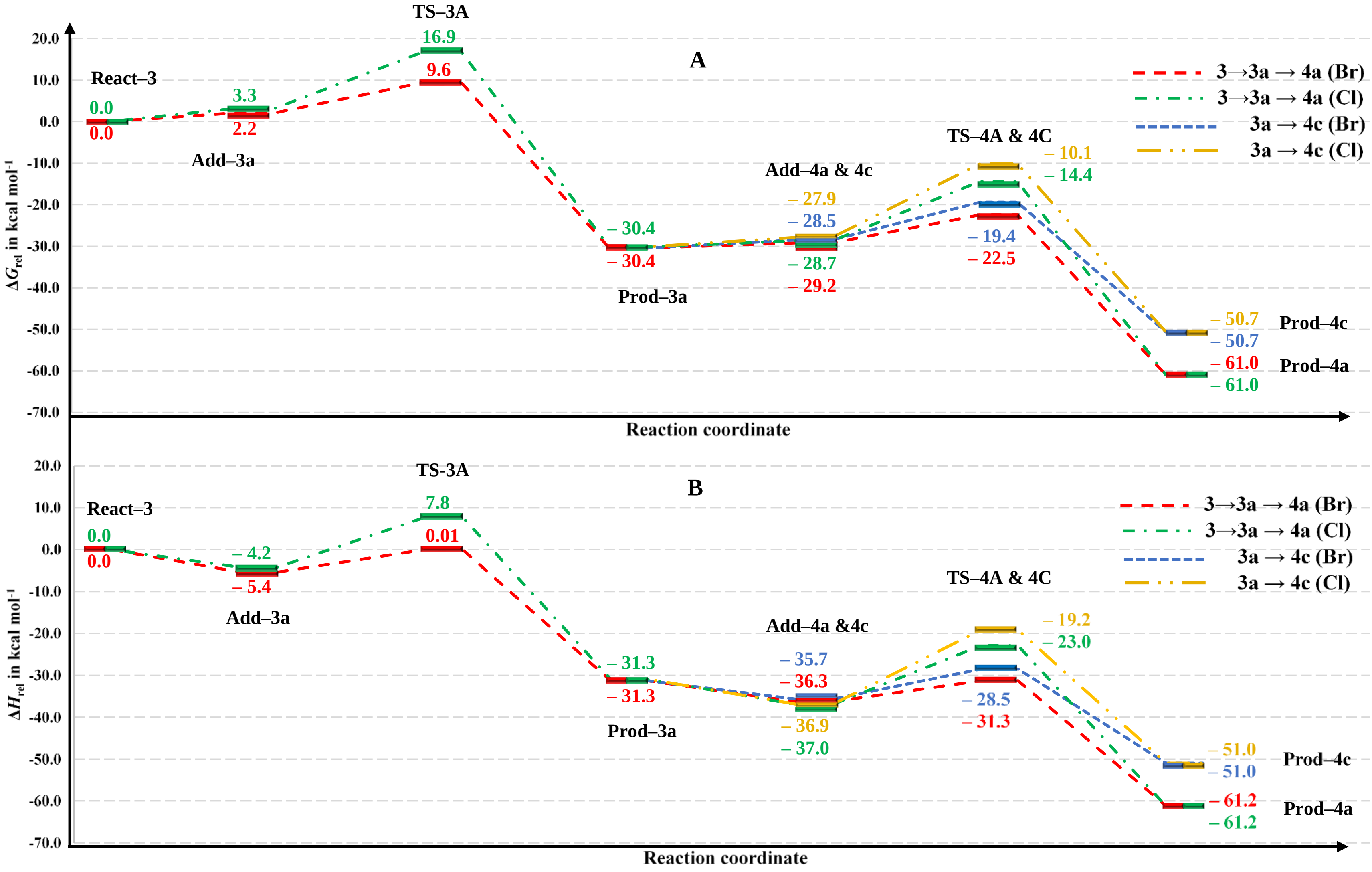


Figure 5.19. The complete overall reaction free energy (A) and enthalpy (B) profiles for the reactions of: **React–3** + 2–X–thiophene → **Prod–3a, Prod–3a** + 2–X–thiophene → **Prod–4a** and **Prod–3a** + 3–X–thiophene → **Prod–4c** at 195.15K**,** implementing a HSM.

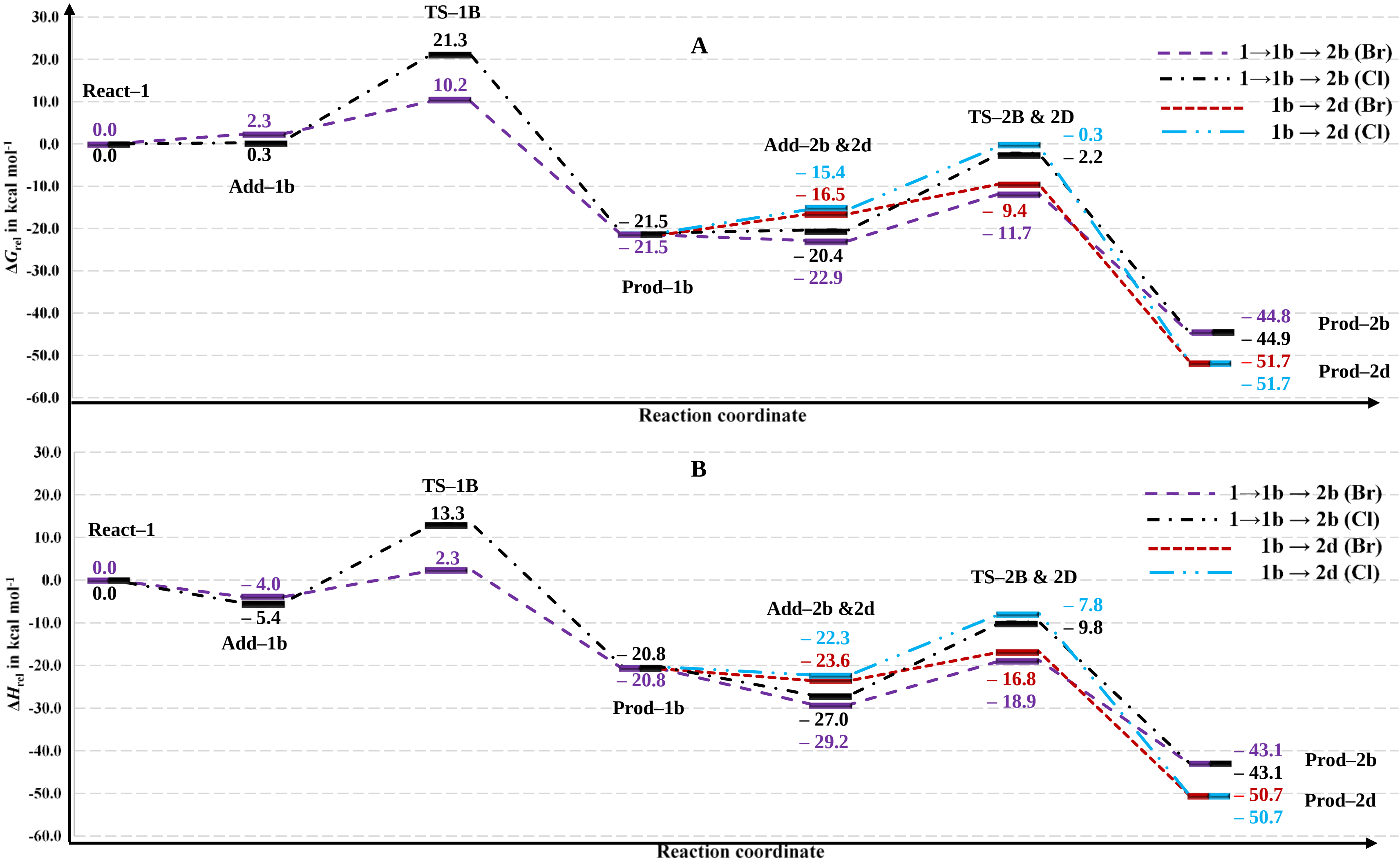


Figure 5.20. The complete overall reaction free energy (A) and enthalpy (B) profiles for the reactions of: **React–1** + 3–X–thiophene → **Prod–1b, Prod–1b** + 3–X–thiophene → **Prod–2b** and **Prod–1b** + 2–X–thiophene → **Prod–2d** at 195.15K**,** implementing a CSM.

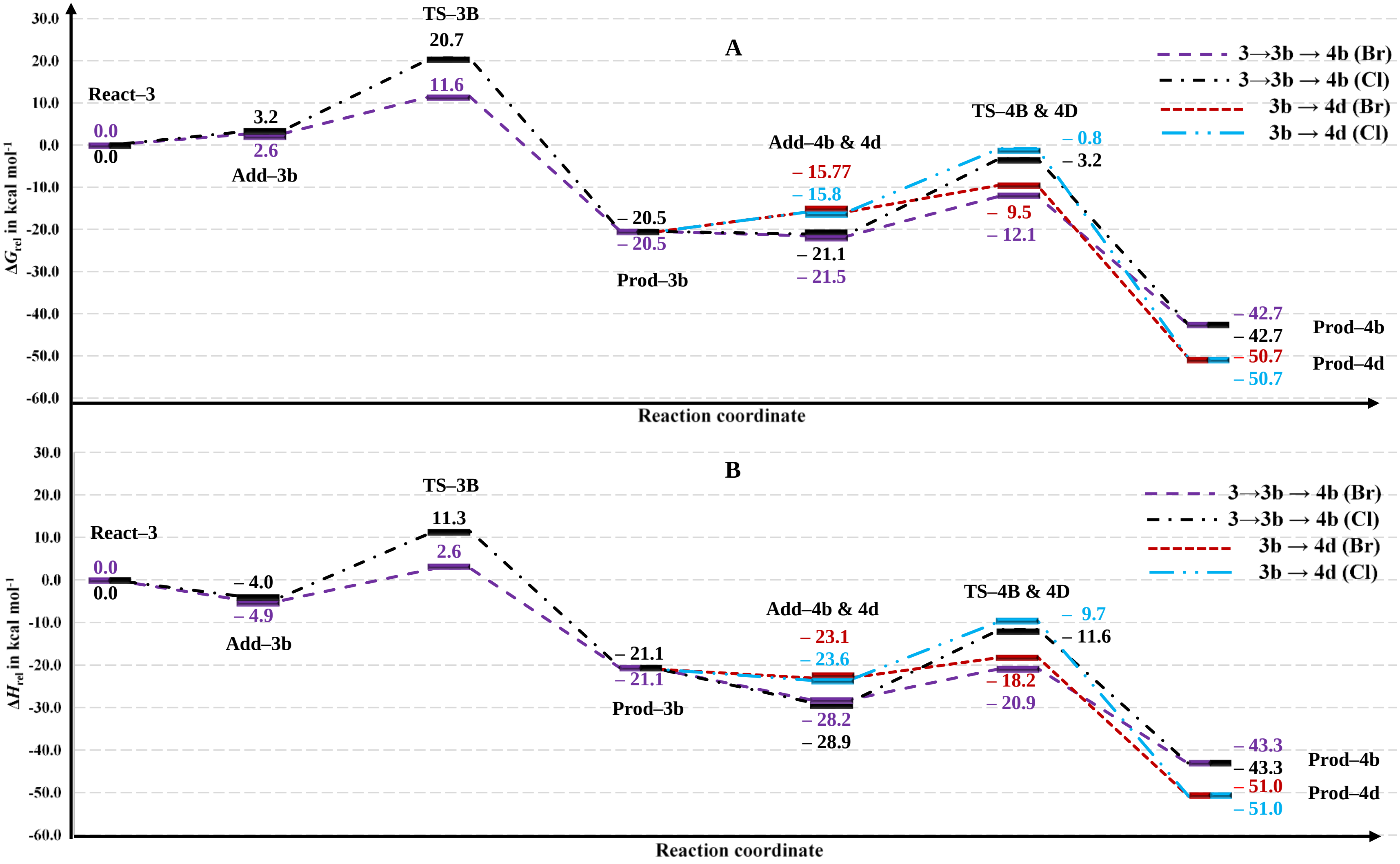


Figure 5.21. The complete overall reaction free energy (A) and enthalpy (B) profiles for the reactions of: **React–3** + 3–X–thiophene → **Prod–3b, Prod–3b** + 3–X–thiophene → **Prod–4b** and **Prod–3b** + 2–X–thiophene → **Prod–4d** at 195.15K**,** implementing a HSM.

5.5. Conclusions

In general, the computed energy terms for the reactions where α-monosubstituted and β-monosubstituted thiophene structures are formed were found to be in accord with experimental data. The favoured position on the thiophene ring, where lithium-halogen exchange occurs, is at the α-carbon. In addition, the reaction systems containing bromine form the more favoured TS structures with relative Gibbs free and enthalpy energy differences of ca. 9 kcal mol^{-1} compared with that of analogue systems with chlorine. Each solvation model adequately defined the reaction profiles for all proposed lithium-halogen exchange reactions. Furthermore, there is no real significant difference in the reaction energy profiles for the equivalent TSs computed with either solvation model. Hence, either solvation model is acceptable for modelling similar reaction systems reported in this work. Inspection of the stable products formed during each reaction shows that lithiated thiophene favours the formation of a homodimer aggregate in THF solution.

The reaction mechanism is defined by the formation of an ate-complex whereby the stability is dependent on both the halogen present and degree of lithium interaction.

5.6. References

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Chapter 6

Conclusions

6.1. *n*-Butyllithium in THF

Starting with a conformational search protocol, which included either a continuum or hybrid solvation model, possible *n*-BuLi oligomers were generated. From the structures, it was evident that THF influences the structural stereochemistry. Though the extent to which the solvent interacts with *n*-BuLi was made very clear after the addition of Grimme's empirical dispersion in the calculations.[1] Furthermore, the comparison of reaction energies between each species resulted in the tetra-solvated dimer and tetramer being the favoured oligomers. With having the reported theoretical work now supporting literature it was intuitive to take it one step further.[2] The next logical step was validating the solvation states via theoretical NMR. From the NMR it was observed that not only does the theoretical NMR compare with the experimental spectra but also it helped in the assigning of chemical shifts. Furthermore, the synergy between the reported experimental and theoretical one-dimensional NMR helped answer any discrepancies found in the literature,[3] such as assignment of the ^{7}Li peaks and confirming that at lower temperatures the proportion of dimer present in solution increase.

From the complete study of *n*-BuLi in THF solution, the theoretical and experimental data effectively shown that computational modelling is an effective technique for investigating similar chemical systems found in this work. Not only for the purpose of generating accurate structures but also for investigation solvent effects, oligomerisation and one-dimensional NMR.

6.2. Reaction Mechanism

Computational techniques successfully managed to model the chemical reactions for twenty-four unique chemical systems. The optimum approach for halogenated thiophene to undergo lithium exchange is allowing the halogen to interact with the anionic α–carbon of *n*-BuLi. Following approach of the two reactants, the reaction mechanism involves the formation of an ate–complex where the stability is influenced by the halogen and degree of lithium interaction. Bromine is significantly more reactive than chlorine in THF due to bromine forming the more stable transition states. The stability arises from the intrinsic properties of bromine, which can better facilitate a negative charge during formation of the ate–complex. Furthermore, the reactions involving exchange at the alpha position are significantly more favoured over the beta position on the thiophene ring.

On completion of the reactions of interest, either 2-lithiothiophene or 3-lithiothiophene were formed. The interesting outcome for the formation of the new organolithium reagents is once again an observation that the system resorts to forming an oligomer. Th stable computed product is that of either a heterodimer or homodimer. The heterodimer consists of *n*-BuLi and lithiated thiophene, where the homodimer is purely lithiated thiophene. This supports the literature which has stated that thiophene, as an organolithium reagent, exists as a mixed-aggregate of dimer and monomer in THF solution.[2b.c]

6.3. Future Studies

From this work, there are certain areas that could/should be investigated further. Firstly, locating and generating a viable TS for the interconversion of solvated *n*-BuLi tetramer to the dimer could be investigated. This would assist in understanding the interconversion mechanism and from the thermodynamic data it would be possible to compare theoretical activation data with that of literature.[3a,4]

Another possible study would be to generate additional experimental 1-D and 2-D NMR at various temperatures in order to help the assignment of the ^{13}C NMR of *n*-BuLi in THF. If a detailed ^{13}C NMR spectra were to be published then maybe the unassigned ^{7}Li peak found at –60°C could be identified.

When it comes to the reaction mechanism, a thorough description of the mechanism has been discussed, although the computational research group has numerous protocols developed and software packages available. Therefore, the reaction TSs can be used for conducting, e.g., AIMALL and IQA calculations to help better understand the electronic environment and density for the stability of the mechanistic ate-complex. In addition, the other techniques can either support or contradict the results reported here. Either way, it is important in science to always question one's own results.

Lastly, *n*-BuLi is used in numerous reactions and take place in several solvents. Therefore, it is recommended that the reaction mechanism protocol found in this work for investigating lithium-halogen exchange, be tested by implementing it on various chemical systems involving different ethereal solvents.

6.4. References

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Appendices

Appendix A:

Supporting Information for Chapter 3

Table A1. Relative uncorrected electronic energies (ΔE), free energies (ΔG) and enthalpies (ΔH) for the lowest energy conformers pertaining to *n*-butyllithium (conformational search). Structures were optimised at the RB3LYP/6-311++G(d,p) level of theory.

***n*-Butyllithium: Monomer**

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
[*n*-BuLi]_1	0.00	[*n*-BuLi]_1	0.00	59.15	[*n*-BuLi]_1	0.00	57.02
[*n*-BuLi]_2	0.47	[*n*-BuLi]_2	0.57	22.70	[*n*-BuLi]_2	0.56	22.32
[*n*-BuLi]_3	0.79	[*n*-BuLi]_3	0.91	12.79	[*n*-BuLi]_3	0.90	12.49
[*n*-BuLi]_4	0.98	[*n*-BuLi]_4	1.52	4.52	[*n*-BuLi]_4	1.21	7.33
[*n*-BuLi]_5	1.06	[*n*-BuLi]_5	2.52	0.84	[*n*-BuLi]_5	2.50	0.84

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
[*n*-BuLi] • 1THF_1	0.00	[*n*-BuLi] • 1THF_4	0.00	42.83	[*n*-BuLi] • 1THF_4	0.00	17.39
[*n*-BuLi] • 1THF_2	0.02	[*n*-BuLi] • 1THF_6	0.42	21.24	[*n*-BuLi] • 1THF_1	0.02	16.92
[*n*-BuLi] • 1THF_3	0.04	[n-BuLi] • 1THF_1	0.85	10.19	[*n*-BuLi] • 1THF_6	0.03	16.62
[*n*-BuLi] • 1THF_4	0.11	[*n*-BuLi] • 1THF_5	0.96	8.42	[*n*-BuLi] • 1THF_2	0.06	15.81
[*n*-BuLi] • 1THF_5	0.18	[*n*-BuLi] • 1THF_2	1.01	7.77	[*n*-BuLi] • 1THF_5	0.08	15.32
[*n*-BuLi] • 1THF_6	0.21	[*n*-BuLi] • 1THF_3	1.07	7.05	[*n*-BuLi] • 1THF_3	0.11	14.56
[*n*-BuLi] • 1THF_7	1.91	[*n*-BuLi] • 1THF_9	1.92	1.68	[*n*-BuLi] • 1THF_10	1.43	1.55
[*n*-BuLi] • 1THF_8	1.93	[*n*-BuLi] • 1THF_8	2.71	0.44	[*n*-BuLi] • 1THF_9	1.95	0.65
[*n*-BuLi] • 1THF_9	1.93	[*n*-BuLi] • 1THF_7	3.12	0.22	[*n*-BuLi] • 1THF_8	1.99	0.60
[*n*-BuLi] • 1THF_10	1.98	[*n*-BuLi] • 1THF_10	3.27	0.17	[*n*-BuLi] • 1THF_7	2.01	0.58

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
[*n*-BuLi] • 2THF_1	0.00	[*n*-BuLi] • 2THF_8	0.00	20.95	[*n*-BuLi] • 2THF_9	0.00	18.63
[*n*-BuLi] • 2THF_2	0.00	[*n*-BuLi] • 2THF_5	0.29	12.88	[*n*-BuLi] • 2THF_8	0.35	10.35
[*n*-BuLi] • 2THF_3	0.02	[*n*-BuLi] • 2THF_4	0.32	12.31	[*n*-BuLi] • 2THF_4	0.39	9.63
[*n*-BuLi] • 2THF_4	0.02	[*n*-BuLi] • 2THF_6	0.33	12.09	[*n*-BuLi] • 2THF_2	0.41	9.36
[*n*-BuLi] • 2THF_5	0.02	[*n*-BuLi] • 2THF_7	0.37	11.14	[*n*-BuLi] • 2THF_6	0.43	9.03
[*n*-BuLi] • 2THF_6	0.02	[*n*-BuLi] • 2THF_10	0.53	8.59	[*n*-BuLi] • 2THF_5	0.43	9.01
[*n*-BuLi] • 2THF_7	0.03	[*n*-BuLi] • 2THF_1	0.67	6.74	[*n*-BuLi] • 2THF_3	0.44	8.90
[*n*-BuLi] • 2THF_8	0.03	[*n*-BuLi] • 2THF_2	0.69	6.56	[*n*-BuLi] • 2THF_7	0.46	8.58
[*n*-BuLi] • 2THF_9	0.05	[*n*-BuLi] • 2THF_9	0.86	4.92	[*n*-BuLi] • 2THF_1	0.48	8.33
[*n*-BuLi] • 2THF_10	0.04	[*n*-BuLi] • 2THF_3	1.01	3.82	[*n*-BuLi] • 2THF_10	0.49	8.18

Table A1 – continued

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
[*n*-BuLi] • 3THF_1	0.00	[*n*-BuLi] • 3THF_1	0.00	43.46	[*n*-BuLi] • 3THF_1	0.00	39.39
[*n*-BuLi] • 3THF_2	0.15	[*n*-BuLi] • 3THF_2	0.22	29.84	[*n*-BuLi] • 3THF_2	0.17	29.62
[*n*-BuLi] • 3THF_3	0.81	[*n*-BuLi] • 3THF_4	0.58	16.31	[*n*-BuLi] • 3THF_4	0.83	9.72
[*n*-BuLi] • 3THF_4	0.81	[*n*-BuLi] • 3THF_3	1.07	7.15	[*n*-BuLi] • 3THF_3	0.86	9.16
[*n*-BuLi] • 3THF_5	1.04	[*n*-BuLi] • 3THF_5	2.03	1.40	[*n*-BuLi] • 3THF_5	1.20	5.23
[*n*-BuLi] • 3THF_6	1.36	[*n*-BuLi] • 3THF_7	2.41	0.74	[*n*-BuLi] • 3THF_6	1.53	2.96
[*n*-BuLi] • 3THF_7	1.62	[*n*-BuLi] • 3THF_8	2.49	0.64	[*n*-BuLi] • 3THF_8	1.77	1.97
[*n*-BuLi] • 3THF_8	1.62	[*n*-BuLi] • 3THF_6	2.71	0.45	[*n*-BuLi] • 3THF_7	1.78	1.95

n-Butyllithium: Dimer

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
$[n\text{-BuLi}]_2$_1	0.00	$[n\text{-BuLi}]_2$_1	0.00	88.11	$[n\text{-BuLi}]_2$_1	0.00	59.60
$[n\text{-BuLi}]_2$_2	0.88	$[n\text{-BuLi}]_2$_3	1.48	7.27	$[n\text{-BuLi}]_2$_2	0.44	28.48
$[n\text{-BuLi}]_2$_3	0.94	$[n\text{-BuLi}]_2$_2	1.75	4.62	$[n\text{-BuLi}]_2$_3	0.95	11.92

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
Boat • 1THF_1	0.00	Boat • 1THF_1	0.00	38.09	Boat • 1THF_1	0.00	37.68
Boat • 1THF_2	0.27	Boat • 1THF_5	0.41	18.93	Boat • 1THF_2	0.27	23.82
Boat • 1THF_3	0.64	Boat • 1THF_2	0.54	15.31	Boat • 1THF_3	0.71	11.40
Boat • 1THF_4	0.95	Boat • 1THF_3	0.75	10.66	Boat • 1THF_5	0.99	7.10
Boat • 1THF_5	1.04	Boat • 1THF_6	0.98	7.25	Boat • 1THF_4	1.14	5.47
Boat • 1THF_6	1.16	Boat • 1THF_7	1.12	5.80	Boat • 1THF_6	1.15	5.39
Boat • 1THF_7	1.19	Boat • 1THF_4	1.71	2.10	Boat • 1THF_7	1.22	4.77
Boat • 1THF_8	1.67	Boat • 1THF_8	1.79	1.86	Boat • 1THF_8	1.28	4.37
Boat • 1THF_9	2.43	Boat • 1THF_9	—	—	Boat • 1THF_9	—	—

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
Chair • 1THF_1	0.00	Chair • 1THF_1	0.00	47.44	Chair • 1THF_1	0.00	50.11
Chair • 1THF_2	0.85	Chair • 1THF_3	0.49	20.80	Chair • 1THF_2	0.68	15.92
Chair • 1THF_3	0.95	Chair • 1THF_5	0.59	17.60	Chair • 1THF_3	0.86	11.72
Chair • 1THF_4	1.29	Chair • 1THF_4	1.09	7.50	Chair • 1THF_5	1.12	7.56
Chair • 1THF_5	1.32	Chair • 1THF_7	1.53	3.58	Chair • 1THF_4	1.27	5.86
Chair • 1THF_6	1.65	Chair • 1THF_6	1.95	1.77	Chair • 1THF_8	1.59	3.42
Chair • 1THF_7	1.70	Chair • 1THF_2	2.36	0.89	Chair • 1THF_6	1.75	2.60
Chair • 1THF_8	1.76	Chair • 1THF_8	3.13	0.24	Chair • 1THF_7	1.96	1.82
Chair • 1THF_9	2.14	Chair • 1THF_9	3.30	0.18	Chair • 1THF_9	2.33	0.98
Chair • 1THF_10	2.47	Chair • 1THF_10	—	—	Chair • 1THF_10	—	—

Table A1 – continued

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
Boat • 2THF_1	0.00	Boat • 2THF_1	0.00	69.18	Boat • 2THF_1	0.00	60.03
Boat • 2THF_2	0.78	Boat • 2THF_3	0.91	14.95	Boat • 2THF_3	0.83	14.68
Boat • 2THF_3	0.83	Boat • 2THF_4	0.90	15.06	Boat • 2THF_4	0.83	14.68
Boat • 2THF_4	0.83	Boat • 2THF_2	2.62	0.82	Boat • 2THF_2	1.03	10.60

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
Chair • 2THF_1	0.00	Chair • 2THF_3	0.00	36.30	Chair • 2THF_3	0.00	30.56
Chair • 2THF_2	0.01	Chair • 2THF_2	0.10	30.70	Chair • 2THF_1	0.01	30.21
Chair • 2THF_3	0.01	Chair • 2THF_1	0.23	24.42	Chair • 2THF_2	0.13	24.36
Chair • 2THF_4	0.56	Chair • 2THF_4	1.13	5.35	Chair • 2THF_4	0.71	9.17
Chair • 2THF_5	0.71	Chair • 2THF_5	1.43	3.23	Chair • 2THF_5	0.99	5.70

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
Boat • 4THF_1	0.00	Boat • 4THF_2	0.00	43.39	Boat • 4THF_2	0.00	24.81
Boat • 4THF_2	0.01	Boat • 4THF_3	0.30	25.98	Boat • 4THF_3	0.05	22.82
Boat • 4THF_3	0.02	Boat • 4THF_1	0.86	10.15	Boat • 4THF_1	0.11	20.55
Boat • 4THF_4	0.40	Boat • 4THF_4	0.92	9.19	Boat • 4THF_4	0.73	7.28
Boat • 4THF_5	0.48	Boat • 4THF_5	1.22	5.50	Boat • 4THF_5	0.77	6.75
Boat • 4THF_6	0.89	Boat • 4THF_7	1.72	2.37	Boat • 4THF_8	0.81	6.32
Boat • 4THF_7	0.93	Boat • 4THF_8	2.26	0.95	Boat • 4THF_7	1.10	3.87
Boat • 4THF_8	0.95	Boat • 4THF_10	2.29	0.91	Boat • 4THF_6	1.16	3.50
Boat • 4THF_9	1.09	Boat • 4THF_6	2.32	0.86	Boat • 4THF_9	1.38	2.40
Boat • 4THF_10	1.43	Boat • 4THF_9	2.44	0.71	Boat • 4THF_10	1.59	1.69

Confomers	ΔE	Confomers	ΔG	Boltz%	Confomers	ΔH	Boltz%
Chair • 4THF_1	0.00	Chair • 4THF_1	0.00	69.40	Chair • 4THF_1	0.00	37.98
Chair • 4THF_2	0.63	Chair • 4THF_4	1.12	10.46	Chair • 4THF_4	0.70	11.74
Chair • 4THF_3	0.66	Chair • 4THF_5	1.37	6.86	Chair • 4THF_2	0.75	10.75
Chair • 4THF_4	0.69	Chair • 4THF_2	1.61	4.56	Chair • 4THF_5	0.79	10.03
Chair • 4THF_5	0.70	Chair • 4THF_6	1.65	4.24	Chair • 4THF_3	0.84	9.22
Chair • 4THF_6	0.81	Chair • 4THF_3	2.00	2.37	Chair • 4THF_6	0.97	7.44
Chair • 4THF_7	0.94	Chair • 4THF_7	2.20	1.69	Chair • 4THF_8	0.98	7.26
Chair • 4THF_8	1.24	Chair • 4THF_8	3.04	0.41	Chair • 4THF_7	1.14	5.58
Chair • 4THF_9	2.20	Chair • 4THF_9	—	—	Chair • 4THF_9	—	—
Chair • 4THF_10	3.08	Chair • 4THF_10	—	—	Chair • 4THF_10	—	—

Structures containing at least one negative vibrational mode after frequency calculations are highlighted in RED

Table A2. Cartesian coordinates and energies for the THF structure found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	0.000000	1.180800	0.426220
2	8	O	0.000000	0.000000	1.255220
3	6	C	0.000000	-1.180800	0.426220
4	6	C	-0.307000	-0.703900	-0.994880
5	6	C	0.307000	0.703900	-0.994880
6	1	H	-0.988100	1.653700	0.481720
7	1	H	0.741900	1.879600	0.819820
8	1	H	0.988100	-1.653700	0.481720
9	1	H	-0.741900	-1.879600	0.819820
10	1	H	0.117900	-1.361200	-1.755480
11	1	H	-1.387700	-0.648000	-1.154980
12	1	H	1.387700	0.648000	-1.154980
13	1	H	-0.117900	1.361200	-1.755480

E(RB3LYP) = –232.522455100 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.116134	
Thermal correction to Energy =	0.118794	
Thermal correction to Enthalpy	0.119412	
Thermal correction to Gibbs Free Energy =	0.099531	
Sum of electronic and zero-point Energies =	-232.406321	
Sum of electronic and thermal Energies =	-232.403661	
Sum of electronic and thermal Enthalpies =	-232.403043	
Sum of electronic and thermal Free Energies =	-232.422924	

Table A3. Cartesian coordinates and energies for *n*-BuLi monomer found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.619416	-1.476816	0.000000
2	1	H	-2.153428	-1.107486	0.882728
3	1	H	-1.697396	-2.568954	0.000000
4	1	H	-2.153428	-1.107486	-0.882728
5	6	C	-0.160475	-1.002166	0.000000
6	1	H	0.359426	-1.409894	0.876803
7	1	H	0.359426	-1.409894	-0.876803
8	6	C	0.000000	0.532308	0.000000
9	1	H	-0.552700	0.916622	0.873098
10	1	H	-0.552700	0.916622	-0.873098
11	6	C	1.437103	1.090948	0.000000
12	1	H	1.969673	0.667717	-0.873285
13	1	H	1.969673	0.667717	0.873285
14	3	Li	1.502727	3.189797	0.000000

E(RB3LYP) = –165.423653917 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.117346		
Thermal correction to Energy =		0.121153		
Thermal correction to Enthalpy		0.121771		
Thermal correction to Gibbs Free Energy =		0.099558		
Sum of electronic and zero-point Energies =		-165.306308		
Sum of electronic and thermal Energies =		-165.302501		
Sum of electronic and thermal Enthalpies =		-165.301883		
Sum of electronic and thermal Free Energies =		-165.324096		

Table A4. Cartesian coordinates and energies for *n*-BuLi·THF found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-4.675098	-1.342884	0.384629
2	1	H	-4.543868	-1.412182	1.470206
3	1	H	-4.785280	-2.361655	-0.001192
4	1	H	-5.618028	-0.816438	0.202300
5	6	C	-3.496988	-0.609988	-0.267470
6	1	H	-2.574420	-1.184136	-0.108571
7	1	H	-3.647155	-0.578825	-1.355223
8	6	C	-3.286370	0.822974	0.242671
9	1	H	-3.097648	0.768604	1.326489
10	1	H	-4.262599	1.339104	0.150305
11	6	C	-2.128859	1.568732	-0.453054
12	1	H	-2.069352	2.586932	-0.023132
13	1	H	-2.424034	1.743526	-1.506495
14	3	Li	-0.168035	0.788521	-0.399124
15	6	C	2.557262	-0.276874	-1.174624
16	8	O	1.698226	0.267605	-0.134273
17	6	C	2.403722	0.287309	1.137899
18	6	C	3.866030	0.011924	0.796920
19	6	C	3.748070	-0.888993	-0.441536
20	1	H	1.976876	-0.999195	-1.750927
21	1	H	2.862991	0.543078	-1.831742
22	1	H	2.235109	1.259232	1.603908
23	1	H	1.982563	-0.494926	1.776982
24	1	H	4.382317	0.942271	0.545213
25	1	H	4.397336	-0.461994	1.623389
26	1	H	4.649094	-0.894459	-1.056378
27	1	H	3.527785	-1.918530	-0.146193

E(RB3LYP) = –397.958503163 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.235625		
Thermal correction to Energy =		0.242814		
Thermal correction to Enthalpy		0.243432		
Thermal correction to Gibbs Free Energy =		0.209653		
Sum of electronic and zero-point Energies =		-397.722878		

Sum of electronic and thermal Energies = -397.715689
Sum of electronic and thermal Enthalpies = -397.715071
Sum of electronic and thermal Free Energies = -397.748850

Table A5. Cartesian coordinates and energies for *n*-BuLi·2THF found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	4.149888	-2.568711	-1.053788
2	1	H	4.792489	-1.718612	-0.798588
3	1	H	4.208187	-2.713511	-2.137688
4	1	H	4.579586	-3.456912	-0.578288
5	6	C	2.709288	-2.331709	-0.585488
6	1	H	2.289989	-1.463608	-1.111288
7	1	H	2.087887	-3.188608	-0.879788
8	6	C	2.564488	-2.112409	0.927712
9	1	H	3.167490	-1.229910	1.195912
10	1	H	3.075487	-2.963910	1.421412
11	6	C	1.105989	-1.905907	1.387612
12	1	H	1.110089	-1.761607	2.485712
13	1	H	0.568587	-2.865606	1.249912
14	3	Li	-0.041509	-0.327505	0.530012
15	6	C	-0.310105	2.619295	-0.290988
16	8	O	0.536094	1.518494	0.132612
17	6	C	1.898694	1.983992	0.327312
18	6	C	1.817496	3.508492	0.312612
19	6	C	0.643097	3.758994	-0.645088
20	1	H	-0.919805	2.278196	-1.128588
21	1	H	-0.969604	2.889396	0.540212
22	1	H	2.266794	1.568092	1.265912
23	1	H	2.514094	1.604291	-0.494488
24	1	H	1.584797	3.889593	1.310912
25	1	H	2.749997	3.966991	-0.019788
26	1	H	0.180298	4.738295	-0.513288
27	1	H	0.973497	3.673093	-1.684088
28	6	C	-3.033209	-0.451401	1.080512
29	8	O	-1.987609	-0.371702	0.077512
30	6	C	-2.473310	-0.881302	-1.191788
31	6	C	-3.815011	-1.545700	-0.886788
32	6	C	-4.321910	-0.723799	0.307712
33	1	H	-2.793810	-1.268001	1.769212
34	1	H	-3.043208	0.488899	1.634612
35	1	H	-2.586309	-0.037601	-1.880688
36	1	H	-1.726511	-1.569403	-1.592488
37	1	H	-4.490011	-1.520899	-1.743588
38	1	H	-3.667212	-2.589400	-0.596688
39	1	H	-4.768908	0.213802	-0.034688
40	1	H	-5.059610	-1.253898	0.911912

E(RB3LYP) = –630.48943111 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.353117

Thermal correction to Energy = 0.363854
Thermal correction to Enthalpy 0.364472
Thermal correction to Gibbs Free Energy = 0.321699
Sum of electronic and zero-point Energies = -630.136314
Sum of electronic and thermal Energies = -630.125577
Sum of electronic and thermal Enthalpies = -630.124959
Sum of electronic and thermal Free Energies = -630.167733

Table A6. Cartesian coordinates and energies for *n*-BuLi·3THF found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	5.492973	0.600863	1.532999
2	1	H	5.582579	1.382042	0.769519
3	1	H	5.722184	-0.355441	1.049393
4	1	H	6.267803	0.784468	2.285050
5	6	C	4.085166	0.586908	2.143953
6	1	H	4.031366	-0.183839	2.924543
7	1	H	3.895830	1.542533	2.650788
8	6	C	2.951416	0.338704	1.123452
9	1	H	3.178193	-0.612992	0.613032
10	1	H	3.052574	1.106524	0.337058
11	6	C	1.504976	0.316972	1.645377
12	1	H	1.320218	1.274145	2.176930
13	1	H	1.438786	-0.452401	2.443183
14	3	Li	-0.089013	0.020025	0.216803
15	6	C	-0.054863	-1.569005	-2.465989
16	8	O	0.034933	-1.595790	-1.020403
17	6	C	0.812516	-2.740274	-0.591900
18	6	C	1.547630	-3.226156	-1.838634
19	6	C	0.541825	-2.891980	-2.950565
20	1	H	-1.103505	-1.442277	-2.744649
21	1	H	0.511829	-0.706701	-2.828937
22	1	H	1.468820	-2.409521	0.214160
23	1	H	0.128540	-3.505732	-0.206738
24	1	H	2.475180	-2.663613	-1.978575
25	1	H	1.794987	-4.287789	-1.786839
26	1	H	1.002226	-2.799408	-3.935610
27	1	H	-0.230828	-3.664028	-3.006474
28	6	C	-2.910140	-1.232808	0.721399
29	8	O	-1.939387	-0.210422	1.052078
30	6	C	-2.133925	0.237730	2.416792
31	6	C	-3.007878	-0.827966	3.072852
32	6	C	-3.886840	-1.284220	1.898252
33	1	H	-3.386658	-0.964770	-0.224405
34	1	H	-2.379921	-2.180802	0.589693
35	1	H	-1.149068	0.354860	2.869056
36	1	H	-2.638313	1.211196	2.399038
37	1	H	-2.391657	-1.655902	3.435053
38	1	H	-3.582267	-0.434215	3.913126
39	1	H	-4.312849	-2.279338	2.036611
40	1	H	-4.708846	-0.579129	1.745014
41	6	C	-1.728310	1.918117	-1.605995

42	8	O	-0.424397	1.535907	-1.103389
43	6	C	0.464382	2.678528	-1.109278
44	6	C	-0.449890	3.897575	-1.188213
45	6	C	-1.598750	3.374375	-2.064039
46	1	H	-2.002744	1.237407	-2.415751
47	1	H	-2.449072	1.802843	-0.791669
48	1	H	1.071140	2.623842	-0.205447
49	1	H	1.120997	2.614503	-1.985427
50	1	H	-0.816003	4.163152	-0.192286
51	1	H	0.052449	4.768412	-1.613036
52	1	H	-2.528972	3.929882	-1.934551
53	1	H	-1.318871	3.420282	-3.120328

E(RB3LYP) = –863.017235668 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.470612		
Thermal correction to Energy =		0.484736		
Thermal correction to Enthalpy		0.485354		
Thermal correction to Gibbs Free Energy =		0.434517		
Sum of electronic and zero-point Energies =		-862.546623		
Sum of electronic and thermal Energies =		-862.532500		
Sum of electronic and thermal Enthalpies =		-862.531882		
Sum of electronic and thermal Free Energies =		-862.582719		

Table A7. Cartesian coordinates and energies for (*n*-BuLi)$_2$ found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	-3.483309	1.314536	-0.326904
2	1	H	-3.832823	1.641384	0.658983
3	1	H	-4.003908	1.918093	-1.077276
4	1	H	-2.417608	1.549670	-0.390943
5	6	C	-3.744411	-0.182087	-0.527643
6	1	H	-4.826592	-0.355873	-0.465842
7	1	H	-3.452665	-0.471154	-1.546753
8	6	C	-3.024013	-1.104778	0.475123
9	1	H	-3.531961	-2.084262	0.430409
10	1	H	-3.234881	-0.724422	1.487302
11	6	C	-1.494773	-1.215415	0.266126
12	1	H	-1.341687	-1.809194	-0.660958
13	1	H	-1.109209	-1.906233	1.045441
14	3	Li	-0.267418	0.187155	1.388691
15	6	C	4.597728	-0.760711	-0.292767
16	1	H	5.318356	0.061445	-0.354255
17	1	H	4.882570	-1.507576	-1.040578
18	1	H	4.708523	-1.221619	0.694710
19	6	C	3.165597	-0.258811	-0.508470
20	1	H	3.082594	0.170158	-1.516662
21	1	H	2.474321	-1.111961	-0.483419
22	6	C	2.704989	0.788540	0.515275
23	1	H	3.459414	1.596783	0.515580
24	1	H	2.778717	0.332663	1.515143

25	6	C	1.263115	1.295594	0.275566
26	1	H	1.272819	1.881756	-0.666921
27	1	H	1.051959	2.077192	1.032981
28	3	Li	-0.128407	0.046827	-0.866947

E(RB3LYP) = –330.867583405 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.238810	
Thermal correction to Energy =	0.246406	
Thermal correction to Enthalpy	0.247024	
Thermal correction to Gibbs Free Energy =	0.214205	
Sum of electronic and zero-point Energies =	-330.628773	
Sum of electronic and thermal Energies =	-330.621178	
Sum of electronic and thermal Enthalpies =	-330.620560	
Sum of electronic and thermal Free Energies =	-330.653379	

Table A8. Cartesian coordinates and energies for (*n*-BuLi)$_2$·1THF (boat conformation) found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	4.517499	-2.018413	-1.500592
2	1	H	4.273901	-1.284313	-2.276292
3	1	H	4.607897	-2.995314	-1.986392
4	1	H	5.501700	-1.756516	-1.097992
5	6	C	3.453199	-2.028811	-0.397492
6	1	H	2.489898	-2.336909	-0.825292
7	1	H	3.713897	-2.794112	0.346508
8	6	C	3.274002	-0.682311	0.318208
9	1	H	2.981404	0.061790	-0.439192
10	1	H	4.275803	-0.361413	0.660208
11	6	C	2.219702	-0.719508	1.448208
12	1	H	2.201404	0.281792	1.924208
13	1	H	2.630101	-1.356009	2.259708
14	3	Li	0.191503	-0.042804	0.906408
15	6	C	-4.519902	-2.410294	-1.142492
16	1	H	-4.415900	-1.607394	-1.880692
17	1	H	-5.589802	-2.557391	-0.963092
18	1	H	-4.132204	-3.327395	-1.599592
19	6	C	-3.763201	-2.074695	0.148508
20	1	H	-4.192899	-1.171794	0.602008
21	1	H	-3.911703	-2.879095	0.880908
22	6	C	-2.249500	-1.856599	-0.045292
23	1	H	-2.123599	-1.066099	-0.802692
24	1	H	-1.841702	-2.763700	-0.519592
25	6	C	-1.428600	-1.510500	1.214108
26	1	H	-1.618901	-2.309300	1.961808
27	1	H	-1.901698	-0.624999	1.687408
28	3	Li	0.620299	-2.212505	1.425708
29	6	C	-1.427191	2.262400	-0.208292
30	8	O	-0.144493	1.762197	0.258508
31	6	C	0.850910	2.821095	0.213408

32	6	C	0.216112	3.944196	-0.602592
33	6	C	-1.275588	3.780299	-0.274292
34	1	H	-1.626092	1.832100	-1.194792
35	1	H	-2.196692	1.925501	0.487708
36	1	H	1.064810	3.137194	1.239208
37	1	H	1.760309	2.412393	-0.229092
38	1	H	0.611714	4.923695	-0.330292
39	1	H	0.391512	3.787696	-1.670592
40	1	H	-1.504887	4.230500	0.695608
41	1	H	-1.932387	4.226301	-1.022492

E(RB3LYP) = –563.405394455 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.356450		
Thermal correction to Energy =		0.367667		
Thermal correction to Enthalpy		0.368285		
Thermal correction to Gibbs Free Energy =		0.325749		
Sum of electronic and zero-point Energies =		-563.048944		
Sum of electronic and thermal Energies =		-563.037728		
Sum of electronic and thermal Enthalpies =		-563.037110		
Sum of electronic and thermal Free Energies =		-563.079646		

Table A9. Cartesian coordinates and energies for (*n*-BuLi)$_2$·1THF (chair conformation) found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-5.225803	-1.790411	0.361104
2	1	H	-5.192402	-2.579411	1.120504
3	1	H	-6.146103	-1.926212	-0.216196
4	1	H	-5.304105	-0.832811	0.887604
5	6	C	-3.978403	-1.830009	-0.530496
6	1	H	-3.941202	-2.786809	-1.067696
7	1	H	-4.054205	-1.053309	-1.302796
8	6	C	-2.653104	-1.640607	0.233704
9	1	H	-2.614002	-2.410807	1.021204
10	1	H	-2.722505	-0.687307	0.782904
11	6	C	-1.351204	-1.672505	-0.595196
12	1	H	-1.441805	-0.911805	-1.395696
13	1	H	-1.341502	-2.625205	-1.164596
14	3	Li	0.373698	-2.549102	0.391904
15	6	C	4.996297	-1.765395	-0.995096
16	1	H	5.020095	-0.800295	-1.512796
17	1	H	5.251898	-2.539394	-1.725896
18	1	H	5.786797	-1.751094	-0.237496
19	6	C	3.624297	-2.015497	-0.358896
20	1	H	2.861997	-2.069798	-1.147596
21	1	H	3.627898	-3.000197	0.128704
22	6	C	3.204895	-0.954398	0.668804
23	1	H	3.170494	0.016302	0.149104
24	1	H	4.034095	-0.858596	1.394604
25	6	C	1.836996	-1.240900	1.328904

26	1	H	1.640594	-0.435400	2.063804
27	1	H	1.967097	-2.130100	1.981304
28	3	Li	0.152394	-0.293102	0.249504
29	6	C	0.803090	2.616199	0.758004
30	8	O	-0.026209	1.640297	0.070404
31	6	C	-0.992210	2.316196	-0.780396
32	6	C	-0.925712	3.790096	-0.385996
33	6	C	0.537888	3.944298	0.054004
34	1	H	0.499590	2.648298	1.809204
35	1	H	1.839690	2.282200	0.697204
36	1	H	-0.698610	2.162096	-1.823296
37	1	H	-1.968809	1.858994	-0.615196
38	1	H	-1.198513	4.448495	-1.211896
39	1	H	-1.599013	3.993295	0.451404
40	1	H	1.190187	4.052299	-0.817096
41	1	H	0.701586	4.798398	0.712604

E(RB3LYP) = –563.405474941 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.356308		
Thermal correction to Energy =		0.367557		
Thermal correction to Enthalpy		0.368175		
Thermal correction to Gibbs Free Energy =		0.325497		
Sum of electronic and zero-point Energies =		-563.049167		
Sum of electronic and thermal Energies =		-563.037918		
Sum of electronic and thermal Enthalpies =		-563.037300		
Sum of electronic and thermal Free Energies =		-563.079978		

Table A10. Cartesian coordinates and energies for (*n*-BuLi)$_2$·2THF (boat conformation) found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	0.534852	-5.378119	0.540007
2	1	H	1.409852	-5.164275	1.163762
3	1	H	0.634015	-6.404813	0.172809
4	1	H	-0.346407	-5.343487	1.190196
5	6	C	0.416095	-4.367282	-0.607481
6	1	H	1.296733	-4.447500	-1.258495
7	1	H	-0.446912	-4.624190	-1.235775
8	6	C	0.275569	-2.902332	-0.147379
9	1	H	1.129291	-2.681190	0.512731
10	1	H	-0.607539	-2.844644	0.509238
11	6	C	0.176100	-1.828737	-1.249023
12	1	H	-0.677480	-2.104963	-1.903986
13	1	H	1.047762	-1.963996	-1.924244
14	3	Li	-1.129145	-0.083186	-0.974906
15	6	C	-0.723635	5.366210	0.578205
16	1	H	0.113928	5.338886	1.284098
17	1	H	-1.631791	5.118784	1.139121
18	1	H	-0.824419	6.397760	0.225350
19	6	C	-0.503768	4.382997	-0.578264

20	1	H	-1.340364	4.456023	-1.285577
21	1	H	0.392931	4.673515	-1.141480
22	6	C	-0.356584	2.912515	-0.138380
23	1	H	-1.254476	2.651221	0.444377
24	1	H	0.470577	2.866274	0.588351
25	6	C	-0.134294	1.866965	-1.249236
26	1	H	0.752604	2.187944	-1.835614
27	1	H	-0.960507	1.982805	-1.982834
28	3	Li	1.151036	0.119440	-0.941166
29	6	C	3.785914	-0.876646	0.188569
30	8	O	2.931974	0.251107	-0.142372
31	6	C	3.620018	1.499054	0.145133
32	6	C	4.854806	1.110031	0.955426
33	6	C	5.177280	-0.287019	0.404871
34	1	H	3.400005	-1.346142	1.098711
35	1	H	3.733221	-1.595032	-0.630666
36	1	H	3.891784	1.969777	-0.804961
37	1	H	2.928811	2.152191	0.679413
38	1	H	5.671044	1.822478	0.827220
39	1	H	4.612321	1.054616	2.020396
40	1	H	5.712679	-0.209136	-0.545547
41	1	H	5.777749	-0.890434	1.087270
42	6	C	-3.137719	-0.302769	1.280677
43	8	O	-2.905888	-0.196745	-0.148557
44	6	C	-4.162299	-0.296733	-0.869253
45	6	C	-5.254539	-0.172843	0.191088
46	6	C	-4.578909	-0.786281	1.426906
47	1	H	-2.398846	-0.991134	1.694291
48	1	H	-2.993867	0.686081	1.727695
49	1	H	-4.188141	0.495273	-1.619716
50	1	H	-4.196108	-1.268195	-1.373061
51	1	H	-5.496166	0.878486	0.370017
52	1	H	-6.169981	-0.690160	-0.099656
53	1	H	-5.027564	-0.462444	2.367135
54	1	H	-4.622418	-1.878099	1.383892

E(RB3LYP) = –795.939168801 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.474136	
Thermal correction to Energy =	0.488950	
Thermal correction to Enthalpy	0.489568	
Thermal correction to Gibbs Free Energy =	0.436490	
Sum of electronic and zero-point Energies =	-795.465033	
Sum of electronic and thermal Energies =	-795.450218	
Sum of electronic and thermal Enthalpies =	-795.449600	
Sum of electronic and thermal Free Energies =	-795.502679	

Table A11. Cartesian coordinates and energies for (*n*-BuLi)$_2$·2THF (chair conformation) found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.060346	4.765387	-0.416207
2	1	H	-1.392153	4.169749	-1.271258
3	1	H	-0.979336	5.806114	-0.745940
4	1	H	-1.847680	4.719733	0.345182
5	6	C	0.268143	4.244916	0.141526
6	1	H	1.045713	4.338175	-0.628537
7	1	H	0.578975	4.893167	0.974044
8	6	C	0.221579	2.774480	0.621788
9	1	H	-0.562368	2.707397	1.394202
10	1	H	1.161480	2.586040	1.164638
11	6	C	0.008203	1.670376	-0.435773
12	1	H	0.785762	1.793370	-1.215464
13	1	H	-0.930026	1.884872	-0.980446
14	3	Li	-1.142151	-0.066620	0.271724
15	6	C	0.353287	-4.812703	-1.205674
16	1	H	1.062251	-5.044006	-2.007168
17	1	H	-0.653642	-4.839370	-1.636445
18	1	H	0.414785	-5.618414	-0.466364
19	6	C	0.642560	-3.450274	-0.565577
20	1	H	1.668883	-3.447020	-0.173958
21	1	H	0.611550	-2.669325	-1.336497
22	6	C	-0.322743	-3.072187	0.567297
23	1	H	-0.317853	-3.911017	1.289008
24	1	H	-1.341110	-3.067200	0.147716
25	6	C	-0.018169	-1.699814	1.210180
26	1	H	0.937959	-1.799417	1.763854
27	1	H	-0.751900	-1.541120	2.026472
28	3	Li	1.143462	-0.100666	0.227585
29	6	C	4.045179	-0.835209	0.779347
30	8	O	3.094844	-0.000306	0.064868
31	6	C	3.800526	0.999432	-0.720011
32	6	C	5.251515	0.944223	-0.247137
33	6	C	5.406115	-0.528798	0.159411
34	1	H	4.014817	-0.565188	1.839943
35	1	H	3.733215	-1.874539	0.668656
36	1	H	3.708853	0.732912	-1.777676
37	1	H	3.317672	1.963028	-0.554126
38	1	H	5.949588	1.251035	-1.027421
39	1	H	5.397049	1.596493	0.618512
40	1	H	5.573895	-1.153276	-0.722581
41	1	H	6.224901	-0.698682	0.860128
42	6	C	-3.899754	0.747609	-0.713985
43	8	O	-3.095102	-0.137025	0.111085
44	6	C	-3.950015	-1.086364	0.805244
45	6	C	-5.377490	-0.585987	0.594046
46	6	C	-5.281744	0.102643	-0.775587
47	1	H	-3.933900	1.731960	-0.236421
48	1	H	-3.412245	0.841779	-1.685176
49	1	H	-3.796743	-2.074876	0.361672
50	1	H	-3.644663	-1.117331	1.852218

51	1	H	-6.104910	-1.398687	0.617675
52	1	H	-5.647827	0.138698	1.367128
53	1	H	-5.322884	-0.637503	-1.579649
54	1	H	-6.071053	0.836583	-0.944808

E(RB3LYP) = –795.937507495 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.473987	
Thermal correction to Energy =	0.488838	
Thermal correction to Enthalpy	0.489456	
Thermal correction to Gibbs Free Energy =	0.436933	
Sum of electronic and zero-point Energies =	-795.463521	
Sum of electronic and thermal Energies =	-795.448670	
Sum of electronic and thermal Enthalpies =	-795.448052	
Sum of electronic and thermal Free Energies =	-795.500574	

Table A12. Cartesian coordinates and energies for (n-BuLi)$_2$·4THF (boat conformation) found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	-0.972910	-3.081896	-4.500101
2	1	H	-0.374949	-3.887417	-4.059301
3	1	H	-0.898604	-3.173357	-5.588929
4	1	H	-2.017723	-3.262696	-4.224049
5	6	C	-0.501033	-1.709157	-4.002972
6	1	H	0.534995	-1.538772	-4.325676
7	1	H	-1.097448	-0.920404	-4.480722
8	6	C	-0.577141	-1.529555	-2.472018
9	1	H	0.014945	-2.340573	-2.018066
10	1	H	-1.614547	-1.741104	-2.167604
11	6	C	-0.134074	-0.171252	-1.895017
12	1	H	-0.753727	0.614673	-2.371986
13	1	H	0.882598	0.033560	-2.289197
14	3	Li	-1.183816	0.080861	0.071292
15	6	C	1.173577	-2.879711	4.606118
16	1	H	0.603291	-3.729261	4.213991
17	1	H	1.129279	-2.928447	5.699318
18	1	H	2.218859	-3.024579	4.311176
19	6	C	0.627146	-1.551877	4.065106
20	1	H	-0.407816	-1.415289	4.406470
21	1	H	1.197746	-0.718219	4.495990
22	6	C	0.661349	-1.433743	2.526304
23	1	H	0.102189	-2.292053	2.120066
24	1	H	1.701874	-1.605859	2.207831
25	6	C	0.136492	-0.126735	1.902306
26	1	H	0.703686	0.713059	2.351667
27	1	H	-0.892922	0.027918	2.286634
28	3	Li	1.180290	0.117433	-0.072486
29	6	C	2.984608	-2.242395	-0.994346
30	8	O	2.881398	-0.981059	-0.294160
31	6	C	4.093956	-0.727121	0.455975

32	6	C	4.936084	-2.000001	0.342661
33	6	C	4.472562	-2.582754	-1.001056
34	1	H	2.403394	-2.998070	-0.453911
35	1	H	2.552958	-2.110458	-1.986964
36	1	H	4.598090	0.135770	0.009653
37	1	H	3.820330	-0.480415	1.483844
38	1	H	6.006401	-1.790025	0.376509
39	1	H	4.697538	-2.689969	1.156800
40	1	H	4.975649	-2.079353	-1.831891
41	1	H	4.652620	-3.655362	-1.090566
42	6	C	-2.896335	-2.321578	1.028142
43	8	O	-2.847511	-1.067359	0.309243
44	6	C	-4.054453	-0.894745	-0.472663
45	6	C	-4.836266	-2.204168	-0.341879
46	6	C	-4.365023	-2.735957	1.020497
47	1	H	-2.270303	-3.054932	0.507409
48	1	H	-2.485417	-2.152299	2.023909
49	1	H	-4.610260	-0.046883	-0.060179
50	1	H	-3.771629	-0.661968	-1.501326
51	1	H	-5.914756	-2.046197	-0.394086
52	1	H	-4.554887	-2.899480	-1.137582
53	1	H	-4.905146	-2.241914	1.833494
54	1	H	-4.492962	-3.814247	1.129325
55	6	C	-2.061829	2.971811	-0.836138
56	8	O	-2.154590	1.908356	0.140913
57	6	C	-2.862029	2.372799	1.315626
58	6	C	-2.972877	3.889672	1.164921
59	6	C	-3.026623	4.057450	-0.360924
60	1	H	-1.028562	3.334113	-0.861646
61	1	H	-2.309954	2.559296	-1.815100
62	1	H	-3.850012	1.899358	1.337374
63	1	H	-2.302174	2.057558	2.197329
64	1	H	-3.849337	4.292573	1.675240
65	1	H	-2.084546	4.380975	1.572218
66	1	H	-4.037144	3.860493	-0.730686
67	1	H	-2.728639	5.051957	-0.697436
68	6	C	2.005032	3.018088	0.819443
69	8	O	2.099757	1.969375	-0.173181
70	6	C	2.665373	2.493393	-1.398651
71	6	C	2.670355	4.013570	-1.240763
72	6	C	2.837263	4.179508	0.277099
73	1	H	0.952014	3.295229	0.936065
74	1	H	2.367323	2.623207	1.769899
75	1	H	3.681389	2.098097	-1.510794
76	1	H	2.056198	2.140049	-2.231741
77	1	H	3.466755	4.486684	-1.817689
78	1	H	1.715235	4.434604	-1.567662
79	1	H	3.887492	4.063567	0.560553
80	1	H	2.489529	5.145600	0.647072

E(RB3LYP) = –1260.99096631 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.708592

Thermal correction to Energy = 0.730421

Thermal correction to Enthalpy 0.731039

Thermal correction to Gibbs Free Energy = 0.661991
Sum of electronic and zero-point Energies = -1260.282374
Sum of electronic and thermal Energies = -1260.260545
Sum of electronic and thermal Enthalpies = -1260.259927
Sum of electronic and thermal Free Energies = -1260.328975

Table A13. Cartesian coordinates and energies for (*n*-BuLi)$_2$·4THF (chair conformation) found in Table 3.1. Structure was optimised at the RB3LYP/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.614320	-4.057604	3.571419
2	1	H	-1.577810	-4.398841	4.611385
3	1	H	-1.170801	-4.843960	2.950313
4	1	H	-2.669506	-3.974228	3.288167
5	6	C	-0.883144	-2.722701	3.377138
6	1	H	-1.327380	-1.962598	4.033454
7	1	H	0.161009	-2.826530	3.701313
8	6	C	-0.901381	-2.195948	1.926472
9	1	H	-1.956523	-2.127939	1.615875
10	1	H	-0.475419	-2.987717	1.288205
11	6	C	-0.187166	-0.861820	1.646426
12	1	H	0.853199	-0.962015	2.016929
13	1	H	-0.625732	-0.098123	2.321660
14	3	Li	-1.205622	0.134968	-0.090311
15	6	C	1.483775	4.420612	-3.304927
16	1	H	1.007643	5.145753	-2.635413
17	1	H	1.447110	4.833971	-4.318463
18	1	H	2.538143	4.351703	-3.014635
19	6	C	0.795734	3.052000	-3.215149
20	1	H	-0.247941	3.144187	-3.544547
21	1	H	1.271757	2.355877	-3.918706
22	6	C	0.816034	2.421480	-1.806867
23	1	H	0.357821	3.147139	-1.115451
24	1	H	1.868801	2.359697	-1.488735
25	6	C	0.139225	1.048574	-1.641678
26	1	H	0.587264	0.363281	-2.389993
27	1	H	-0.907049	1.157697	-1.995454
28	3	Li	1.169998	-0.074130	0.021685
29	6	C	2.652306	-2.802848	-0.062828
30	8	O	2.391217	-1.534468	-0.708068
31	6	C	3.048884	-1.487425	-1.998616
32	6	C	3.937724	-2.730786	-2.063193
33	6	C	3.182337	-3.719621	-1.162754
34	1	H	3.399097	-2.652040	0.725576
35	1	H	1.723395	-3.144956	0.393965
36	1	H	2.279639	-1.495934	-2.776507
37	1	H	3.605819	-0.550716	-2.069403
38	1	H	4.068546	-3.090179	-3.085162
39	1	H	4.926881	-2.518183	-1.647476
40	1	H	2.353242	-4.178491	-1.709049
41	1	H	3.816187	-4.516037	-0.769177
42	6	C	-3.655014	-0.608769	-1.844785
43	8	O	-2.493978	-1.088009	-1.122083

44	6	C	-2.049358	-2.344513	-1.682767
45	6	C	-3.243475	-2.882629	-2.465220
46	6	C	-3.873862	-1.588609	-3.001671
47	1	H	-4.504391	-0.600783	-1.154325
48	1	H	-3.461972	0.413201	-2.176311
49	1	H	-1.730052	-2.981235	-0.857540
50	1	H	-1.192785	-2.157728	-2.340626
51	1	H	-2.945887	-3.575971	-3.253880
52	1	H	-3.936709	-3.400240	-1.795526
53	1	H	-3.340949	-1.251162	-3.894819
54	1	H	-4.929846	-1.695228	-3.255642
55	6	C	-3.545789	1.140812	1.626962
56	8	O	-2.585541	1.473379	0.594047
57	6	C	-2.414640	2.908486	0.518648
58	6	C	-3.591366	3.502678	1.288842
59	6	C	-3.825290	2.443909	2.377335
60	1	H	-4.448921	0.752271	1.144305
61	1	H	-3.115323	0.358555	2.254435
62	1	H	-1.457745	3.174481	0.980302
63	1	H	-2.385284	3.191221	-0.534510
64	1	H	-3.365946	4.491847	1.690953
65	1	H	-4.469571	3.587358	0.642108
66	1	H	-3.111062	2.575453	3.195054
67	1	H	-4.832388	2.470352	2.796658
68	6	C	2.169157	2.202689	1.788124
69	8	O	2.574475	1.054622	1.001925
70	6	C	3.903531	0.638110	1.382128
71	6	C	4.505760	1.826862	2.127178
72	6	C	3.272666	2.417311	2.827763
73	1	H	2.072369	3.057858	1.112663
74	1	H	1.194155	1.987723	2.229330
75	1	H	3.831988	-0.243059	2.030827
76	1	H	4.444111	0.363812	0.475186
77	1	H	5.293201	1.527147	2.820906
78	1	H	4.926896	2.546757	1.419303
79	1	H	3.052327	1.858785	3.741833
80	1	H	3.389923	3.469574	3.092078

E(RB3LYP) = –1260.99157376 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.708922
Thermal correction to Energy = 0.730702
Thermal correction to Enthalpy 0.731320
Thermal correction to Gibbs Free Energy = 0.662300
Sum of electronic and zero-point Energies = -1260.282652
Sum of electronic and thermal Energies = -1260.260871
Sum of electronic and thermal Enthalpies = -1260.260253
Sum of electronic and thermal Free Energies = -1260.329274

Table A14. Cartesian coordinates and energies for *n*-BuLi·1THF found in Table 3.2. Structure was optimised at the RMP2/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	4.930500	-1.220318	0.003601
2	1	H	4.615997	-1.788917	0.886201
3	1	H	6.024900	-1.172023	0.007501
4	1	H	4.621997	-1.785217	-0.883399
5	6	C	4.292606	0.171884	0.004301
6	1	H	4.627709	0.733683	0.886701
7	1	H	4.633109	0.737083	-0.873899
8	6	C	2.755106	0.141591	-0.000499
9	1	H	2.441103	-0.452007	0.874901
10	1	H	2.446503	-0.450107	-0.878999
11	6	C	2.036512	1.504595	-0.001299
12	1	H	2.408815	2.074393	-0.875199
13	1	H	2.403815	2.073093	0.875601
14	3	Li	-0.083689	1.252204	-0.008799
15	6	C	-2.034799	-1.034987	0.124001
16	8	O	-1.843093	0.397112	-0.009299
17	6	C	-3.129290	1.053418	-0.139799
18	6	C	-4.157095	0.004023	0.262801
19	6	C	-3.493401	-1.281180	-0.241299
20	1	H	-1.322702	-1.534590	-0.536099
21	1	H	-1.831501	-1.315388	1.163001
22	1	H	-3.123886	1.937318	0.501401
23	1	H	-3.260089	1.357619	-1.183899
24	1	H	-4.264595	-0.025777	1.351601
25	1	H	-5.134394	0.193727	-0.186199
26	1	H	-3.886105	-2.185978	0.227401
27	1	H	-3.605701	-1.364580	-1.326699

E(RMP2) = –396.67913289 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.240203		
Thermal correction to Energy =		0.247225		
Thermal correction to Enthalpy		0.247843		
Thermal correction to Gibbs Free Energy =		0.215104		
Sum of electronic and zero-point Energies =		-396.468930		
Sum of electronic and thermal Energies =		-396.431908		
Sum of electronic and thermal Enthalpies =		-396.431290		
Sum of electronic and thermal Free Energies =		-396.464029		

Table A15. Cartesian coordinates and energies for *n*-BuLi·1THF found in Table 3.2. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-3.685244	-1.766550	0.425193
2	1	H	-3.690539	-1.717847	1.519853
3	1	H	-3.364899	-2.773557	0.138442
4	1	H	-4.718910	-1.637600	0.087047
5	6	C	-2.773872	-0.685129	-0.166086
6	1	H	-1.738318	-0.861018	0.156048
7	1	H	-2.766190	-0.772257	-1.261100
8	6	C	-3.176092	0.747906	0.212448
9	1	H	-3.148039	0.823104	1.311170
10	1	H	-4.246579	0.858274	-0.052623
11	6	C	-2.266396	1.828585	-0.410161
12	1	H	-2.620997	2.818996	-0.069386
13	1	H	-2.451670	1.837780	-1.502180
14	3	Li	-0.199582	1.558165	-0.053953
15	6	C	1.880265	-0.305466	-1.083561
16	8	O	1.530689	0.672037	-0.062688
17	6	C	2.508217	0.637103	1.014725
18	6	C	3.655505	-0.228861	0.497720
19	6	C	2.927703	-1.206234	-0.437067
20	1	H	0.968877	-0.827512	-1.379549
21	1	H	2.285331	0.229422	-1.948437
22	1	H	2.800904	1.663258	1.243490
23	1	H	2.033122	0.193504	1.895443
24	1	H	4.368035	0.378632	-0.067056
25	1	H	4.192240	-0.724740	1.307471
26	1	H	3.585468	-1.667724	-1.174753
27	1	H	2.444872	-1.999626	0.140218

E(RB3LYP) = –397.97598134 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.236231		
Thermal correction to Energy =		0.243180		
Thermal correction to Enthalpy		0.243798		
Thermal correction to Gibbs Free Energy =		0.211622		
Sum of electronic and zero-point Energies =		-397.739750		
Sum of electronic and thermal Energies =		-397.732801		
Sum of electronic and thermal Enthalpies =		-397.732183		
Sum of electronic and thermal Free Energies =		-397.764359		

Table A16. Cartesian coordinates and energies for *n*-BuLi·2THF found in Table 3.2. Structure was optimised at the RMP2/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-5.279306	-1.564299	0.158194
2	1	H	-5.331106	-1.287399	1.217394
3	1	H	-6.122607	-2.229698	-0.057006
4	1	H	-5.413406	-0.650199	-0.431706
5	6	C	-3.931807	-2.218200	-0.161606
6	1	H	-3.819908	-3.144000	0.418894
7	1	H	-3.901607	-2.508100	-1.221006
8	6	C	-2.725906	-1.309601	0.130494
9	1	H	-2.795506	-1.013600	1.191394
10	1	H	-2.879705	-0.377400	-0.440506
11	6	C	-1.329607	-1.886702	-0.163706
12	1	H	-1.332507	-2.232102	-1.218106
13	1	H	-1.222707	-2.817102	0.428594
14	3	Li	0.249294	-0.476003	0.074394
15	6	C	-1.143504	1.984298	0.980794
16	8	O	0.086096	1.466797	0.426694
17	6	C	0.559297	2.376797	-0.601306
18	6	C	-0.497803	3.480998	-0.718406
19	6	C	-1.749603	2.807099	-0.143906
20	1	H	-1.745004	1.129099	1.292194
21	1	H	-0.911803	2.613598	1.849394
22	1	H	1.541297	2.756896	-0.307106
23	1	H	0.658496	1.804297	-1.528506
24	1	H	-0.221302	4.340398	-0.100106
25	1	H	-0.620502	3.817298	-1.750106
26	1	H	-2.498403	3.519499	0.210494
27	1	H	-2.206704	2.141899	-0.883506
28	6	C	3.158695	0.169095	0.534794
29	8	O	2.188694	-0.567704	-0.244106
30	6	C	2.798193	-1.784905	-0.750706
31	6	C	4.273594	-1.704506	-0.362506
32	6	C	4.220294	-0.853906	0.910794
33	1	H	3.583896	0.965295	-0.088506
34	1	H	2.635095	0.613195	1.383494
35	1	H	2.299793	-2.634704	-0.273906
36	1	H	2.632393	-1.826705	-1.829606
37	1	H	4.708893	-2.694206	-0.207806
38	1	H	4.845494	-1.184206	-1.137306
39	1	H	3.880094	-1.455806	1.759494
40	1	H	5.175895	-0.388006	1.161994

E(RMP2) = –628.53127272 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.359702		
Thermal correction to Energy =		0.370200		
Thermal correction to Enthalpy		0.370818		
Thermal correction to Gibbs Free Energy =		0.329258		
Sum of electronic and zero-point Energies =		-628.171571		

Sum of electronic and thermal Energies = -628.161073

Sum of electronic and thermal Enthalpies = -628.160455

Sum of electronic and thermal Free Energies = -628.202014

Table A17. Cartesian coordinates and energies for *n*-BuLi·2THF found in Table 3.2. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.056574	-2.839943	-1.869205
2	1	H	-0.008561	-3.072638	-2.089119
3	1	H	-1.457716	-2.277058	-2.718749
4	1	H	-1.598100	-3.790261	-1.814237
5	6	C	-1.177172	-2.058661	-0.557151
6	1	H	-0.656595	-1.098995	-0.659088
7	1	H	-2.230148	-1.804891	-0.376228
8	6	C	-0.627846	-2.800013	0.671111
9	1	H	0.429792	-3.034354	0.471729
10	1	H	-1.133899	-3.786517	0.699043
11	6	C	-0.746078	-1.987140	1.980284
12	1	H	-0.318706	-2.590123	2.801962
13	1	H	-1.822783	-1.907105	2.230287
14	3	Li	0.024044	-0.050557	1.596425
15	6	C	2.468348	1.516251	0.615054
16	8	O	1.721402	0.276296	0.672879
17	6	C	2.390409	-0.745544	-0.117023
18	6	C	3.720192	-0.128613	-0.551837
19	6	C	3.389461	1.371043	-0.591645
20	1	H	1.754280	2.337382	0.534436
21	1	H	3.038845	1.629645	1.543514
22	1	H	2.498647	-1.639345	0.498333
23	1	H	1.751578	-0.983125	-0.972893
24	1	H	4.495036	-0.324493	0.194464
25	1	H	4.060926	-0.521659	-1.510675
26	1	H	4.270688	2.010233	-0.521039
27	1	H	2.852468	1.621515	-1.511354
28	6	C	-2.549527	1.263725	0.983464
29	8	O	-1.114862	1.328509	0.743806
30	6	C	-0.863006	1.812695	-0.597693
31	6	C	-2.169395	1.599961	-1.354436
32	6	C	-3.213115	1.864249	-0.258573
33	1	H	-2.812078	0.212811	1.126242
34	1	H	-2.769534	1.814210	1.900522
35	1	H	-0.597382	2.875060	-0.547153
36	1	H	-0.017626	1.253819	-0.999970
37	1	H	-2.266474	2.268287	-2.211490
38	1	H	-2.236064	0.567510	-1.706440
39	1	H	-3.364536	2.939919	-0.132253
40	1	H	-4.180688	1.405354	-0.466696

E(RB3LYP) = –630.52393083 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.354891

Thermal correction to Energy = 0.364888
Thermal correction to Enthalpy 0.365506
Thermal correction to Gibbs Free Energy = 0.326607
Sum of electronic and zero-point Energies = -630.169040
Sum of electronic and thermal Energies = -630.159043
Sum of electronic and thermal Enthalpies = -630.158425
Sum of electronic and thermal Free Energies = -630.197324

Table A18. Cartesian coordinates and energies for *n*-BuLi·3THF found in Table 3.2. Structure was optimised at the RMP2/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	4.778618	1.512043	1.153092
2	1	H	5.073606	0.524239	0.779892
3	1	H	5.613722	1.913533	1.738192
4	1	H	4.631525	2.165244	0.284992
5	6	C	3.489917	1.412458	1.974892
6	1	H	3.655109	0.771356	2.851892
7	1	H	3.216628	2.404461	2.360692
8	6	C	2.300910	0.852372	1.174392
9	1	H	2.620399	-0.124032	0.770792
10	1	H	2.181518	1.500073	0.286592
11	6	C	0.954408	0.695687	1.901792
12	1	H	0.692020	1.677791	2.346792
13	1	H	1.116400	0.025086	2.769692
14	3	Li	-0.235699	0.102801	0.245092
15	6	C	1.129571	-2.453215	-0.136608
16	8	O	0.539884	-1.348508	-0.868008
17	6	C	1.362988	-1.036317	-2.015108
18	6	C	2.202473	-2.284427	-2.251108
19	6	C	2.469168	-2.741230	-0.812608
20	1	H	1.222075	-2.153716	0.910992
21	1	H	0.450561	-3.310607	-0.215008
22	1	H	0.696291	-0.783309	-2.842608
23	1	H	1.990998	-0.170525	-1.777008
24	1	H	1.618464	-3.038020	-2.789708
25	1	H	3.114676	-2.070738	-2.813308
26	1	H	2.748755	-3.794534	-0.734108
27	1	H	3.259575	-2.130740	-0.365408
28	6	C	-2.585421	-1.754871	-0.026608
29	8	O	-2.174705	-0.419176	0.300992
30	6	C	-2.847301	-0.080868	1.533892
31	6	C	-3.114017	-1.413165	2.271092
32	6	C	-2.550329	-2.480871	1.311992
33	1	H	-3.603820	-1.735059	-0.441108
34	1	H	-1.887125	-2.134979	-0.773708
35	1	H	-2.180893	0.588924	2.080292
36	1	H	-3.782595	0.439043	1.293092
37	1	H	-2.623017	-1.438870	3.245992
38	1	H	-4.187318	-1.556852	2.421792
39	1	H	-1.513332	-2.716883	1.567292
40	1	H	-3.135340	-3.404164	1.310192

41	6	C	-1.396583	1.446715	-2.100608
42	8	O	-0.323782	1.532703	-1.146808
43	6	C	-0.381666	2.873703	-0.636408
44	6	C	-1.870863	3.112521	-0.395408
45	6	C	-2.540673	2.319429	-1.543008
46	1	H	-1.039578	1.829311	-3.065608
47	1	H	-1.659695	0.392518	-2.200008
48	1	H	0.233434	2.904696	0.263592
49	1	H	0.016642	3.564999	-1.392708
50	1	H	-2.151268	2.694224	0.574692
51	1	H	-2.129151	4.174524	-0.404808
52	1	H	-3.359580	1.700338	-1.171208
53	1	H	-2.930965	2.984333	-2.317908

E(RMP2) = –860.38813539 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.479943
Thermal correction to Energy = 0.493317
Thermal correction to Enthalpy 0.493935
Thermal correction to Gibbs Free Energy = 0.446370
Sum of electronic and zero-point Energies = -859.908192
Sum of electronic and thermal Energies = -859.894819
Sum of electronic and thermal Enthalpies = -859.894201
Sum of electronic and thermal Free Energies = -859.941764

Table A19. Cartesian coordinates and energies for *n*-BuLi·3THF found in Table 3.2. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	5.228992	0.866093	1.447897
2	1	H	5.235020	1.689164	0.724213
3	1	H	5.472489	-0.051516	0.900302
4	1	H	6.036245	1.048870	2.165152
5	6	C	3.859712	0.748572	2.130312
6	1	H	3.881910	-0.063923	2.868552
7	1	H	3.648061	1.665854	2.695926
8	6	C	2.692261	0.493376	1.153009
9	1	H	2.946772	-0.412477	0.576959
10	1	H	2.712300	1.307965	0.408634
11	6	C	1.280059	0.357411	1.745158
12	1	H	1.069464	1.269489	2.340676
13	1	H	1.300094	-0.460907	2.494099
14	3	Li	-0.169406	0.027259	0.214353
15	6	C	0.267341	-1.447646	-2.394590
16	8	O	0.138245	-1.556478	-0.953530
17	6	C	1.048530	-2.562797	-0.451453
18	6	C	2.115191	-2.701891	-1.531576
19	6	C	1.287408	-2.512845	-2.812400
20	1	H	-0.718462	-1.596310	-2.842886
21	1	H	0.607430	-0.433949	-2.620218
22	1	H	1.422977	-2.210480	0.509722

23	1	H	0.499279	-3.501761	-0.308271
24	1	H	2.855141	-1.903041	-1.429700
25	1	H	2.632013	-3.662113	-1.489686
26	1	H	1.883842	-2.195646	-3.669219
27	1	H	0.782354	-3.446642	-3.075327
28	6	C	-2.860201	-1.386663	0.328727
29	8	O	-2.078716	-0.245356	0.768133
30	6	C	-2.364290	0.041415	2.158372
31	6	C	-2.932851	-1.257335	2.718994
32	6	C	-3.735401	-1.789114	1.521189
33	1	H	-3.440956	-1.092920	-0.549797
34	1	H	-2.160868	-2.174279	0.038248
35	1	H	-1.428892	0.361516	2.618254
36	1	H	-3.097698	0.855535	2.211577
37	1	H	-2.119666	-1.943420	2.973114
38	1	H	-3.542970	-1.098036	3.609685
39	1	H	-3.906132	-2.866159	1.559277
40	1	H	-4.708000	-1.291560	1.469599
41	6	C	-1.580175	1.692678	-1.852470
42	8	O	-0.330058	1.490575	-1.142752
43	6	C	0.199158	2.769259	-0.721152
44	6	C	-1.020989	3.675500	-0.617523
45	6	C	-1.860525	3.202799	-1.815728
46	1	H	-1.473839	1.303919	-2.868623
47	1	H	-2.346846	1.119258	-1.326972
48	1	H	0.725314	2.603495	0.218373
49	1	H	0.905356	3.134587	-1.477279
50	1	H	-1.547396	3.485053	0.322289
51	1	H	-0.764421	4.735257	-0.663892
52	1	H	-2.924651	3.418659	-1.707989
53	1	H	-1.508123	3.681931	-2.733262

E(RB3LYP) = –863.06791627 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.472030
Thermal correction to Energy = 0.485665
Thermal correction to Enthalpy 0.486283
Thermal correction to Gibbs Free Energy = 0.435818
Sum of electronic and zero-point Energies = -862.595887
Sum of electronic and thermal Energies = -862.582252
Sum of electronic and thermal Enthalpies = -862.581634
Sum of electronic and thermal Free Energies = -862.632098

Table A20. Cartesian coordinates and energy for (n-BuLi)$_2$·2THF (boat conformation) found in Table 3.2. Structure was optimised at the RMP2/6-311++G(d,p) level of theory. Energy value is reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-0.660139	-3.011917	2.132482
2	1	H	0.264783	-2.569795	2.521207
3	1	H	-0.801811	-3.982041	2.621519
4	1	H	-1.489734	-2.359861	2.430507

5	6	C	-0.595342	-3.137374	0.607557
6	1	H	0.233239	-3.800646	0.321633
7	1	H	-1.513957	-3.608316	0.229895
8	6	C	-0.410574	-1.784448	-0.095282
9	1	H	0.482977	-1.306589	0.338823
10	1	H	-1.242424	-1.134975	0.222764
11	6	C	-0.307667	-1.798935	-1.634563
12	1	H	-1.200670	-2.318580	-2.032757
13	1	H	0.526440	-2.476479	-1.909166
14	3	Li	-1.136725	0.200363	-2.044495
15	6	C	0.663810	3.023612	2.126990
16	1	H	1.493720	2.372720	2.426655
17	1	H	-0.260714	2.582992	2.518355
18	1	H	0.806000	3.995599	2.612158
19	6	C	0.597408	3.143247	0.601664
20	1	H	-0.231155	3.805854	0.314135
21	1	H	1.515847	3.612295	0.221222
22	6	C	0.411068	1.787804	-0.095867
23	1	H	-0.482288	1.312147	0.341030
24	1	H	1.242942	1.138991	0.223490
25	6	C	0.306364	1.796675	-1.635035
26	1	H	1.199765	2.313609	-2.036007
27	1	H	-0.526960	2.474545	-1.911223
28	3	Li	1.135502	-0.203095	-2.045206
29	6	C	3.246493	-1.572042	-0.330873
30	8	O	2.886564	-0.482281	-1.195693
31	6	C	3.751045	0.615634	-0.834185
32	6	C	4.058767	0.447793	0.670072
33	6	C	3.420087	-0.911396	1.031816
34	1	H	2.445766	-2.311441	-0.381311
35	1	H	4.186848	-2.018006	-0.682724
36	1	H	4.664156	0.554949	-1.437410
37	1	H	3.216095	1.536136	-1.073181
38	1	H	5.138648	0.433378	0.837686
39	1	H	3.632398	1.262493	1.259489
40	1	H	4.040440	-1.505282	1.707617
41	1	H	2.438884	-0.765446	1.491875
42	6	C	-3.248197	1.568139	-0.331338
43	8	O	-2.888300	0.478101	-1.195815
44	6	C	-3.751724	-0.620258	-0.833065
45	6	C	-4.059578	-0.451137	0.671054
46	6	C	-3.420485	0.908084	1.031780
47	1	H	-2.447842	2.307879	-0.382734
48	1	H	-4.189030	2.013476	-0.682720
49	1	H	-4.664889	-0.561163	-1.436350
50	1	H	-3.215849	-1.540478	-1.071056
51	1	H	-5.139486	-0.436044	0.838469
52	1	H	-3.633720	-1.265592	1.261192
53	1	H	-4.040092	1.502217	1.708043
54	1	H	-2.438781	0.762197	1.490807

E(RMP2) = –793.39932214 Hartree

Table A21. Cartesian coordinates and energies for (*n*-BuLi)$_2$·2THF (boat conformation) found in Table 3.2. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.226342	-3.093380	2.164312
2	1	H	-0.277806	-2.843149	2.652197
3	1	H	-1.565759	-4.052865	2.567561
4	1	H	-1.955594	-2.331364	2.460886
5	6	C	-1.062795	-3.131882	0.640170
6	1	H	-0.347325	-3.916591	0.362422
7	1	H	-2.015396	-3.412388	0.171721
8	6	C	-0.591711	-1.796756	0.035854
9	1	H	0.341662	-1.511489	0.545955
10	1	H	-1.309936	-1.023021	0.347614
11	6	C	-0.389677	-1.752624	-1.493835
12	1	H	-1.306104	-2.151388	-1.970087
13	1	H	0.378849	-2.503455	-1.756363
14	3	Li	-1.144676	0.249574	-1.919285
15	6	C	1.115409	3.229754	2.105221
16	1	H	1.833903	2.465651	2.422076
17	1	H	0.158871	2.998304	2.586756
18	1	H	1.460515	4.192721	2.495159
19	6	C	0.969495	3.242606	0.578851
20	1	H	0.275067	4.037297	0.276967
21	1	H	1.933381	3.493272	0.116662
22	6	C	0.474443	1.906525	-0.003865
23	1	H	-0.482563	1.667221	0.483182
24	1	H	1.155837	1.118807	0.354392
25	6	C	0.320473	1.823426	-1.537843
26	1	H	1.265094	2.179376	-1.993721
27	1	H	-0.414706	2.588399	-1.849394
28	3	Li	1.078514	-0.189420	-1.846368
29	6	C	3.245857	-1.749585	-0.509149
30	8	O	2.863083	-0.497287	-1.143888
31	6	C	3.742437	0.551546	-0.679895
32	6	C	4.093168	0.139148	0.742578
33	6	C	4.252730	-1.384828	0.598126
34	1	H	2.334155	-2.205568	-0.121171
35	1	H	3.677195	-2.409797	-1.265773
36	1	H	4.632810	0.590137	-1.319534
37	1	H	3.202695	1.494418	-0.758354
38	1	H	4.994192	0.629823	1.113920
39	1	H	3.263080	0.382311	1.411022
40	1	H	5.270266	-1.628441	0.283373
41	1	H	4.049352	-1.921452	1.525593
42	6	C	-3.288721	1.682798	-0.421610
43	8	O	-2.947919	0.545023	-1.238897
44	6	C	-3.834465	-0.529136	-0.844878
45	6	C	-4.170241	-0.287659	0.644610
46	6	C	-3.523159	1.082921	0.962369
47	1	H	-2.462364	2.390356	-0.477224
48	1	H	-4.196851	2.154042	-0.818552
49	1	H	-4.731486	-0.489018	-1.471371
50	1	H	-3.310636	-1.465635	-1.030501

51	1	H	-5.251050	-0.260735	0.793130
52	1	H	-3.764534	-1.076905	1.278104
53	1	H	-4.154195	1.715427	1.588509
54	1	H	-2.564844	0.946104	1.467984

E(RB3LYP) =	–795.98979487	Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =	0.476728			
Thermal correction to Energy =	0.490657			
Thermal correction to Enthalpy	0.491275			
Thermal correction to Gibbs Free Energy =	0.442418			
Sum of electronic and zero-point Energies =	-795.513067			
Sum of electronic and thermal Energies =	-795.499138			
Sum of electronic and thermal Enthalpies =	-795.498520			
Sum of electronic and thermal Free Energies =	-795.547377			

Table A22. Cartesian coordinates and energy for (n-BuLi)$_2$·2THF (chair conformation) found in Table 3.2. Structure was optimised at the RMP2/6-311++G(d,p) level of theory. Energy value is reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	-1.332111	4.230410	-1.145668
2	1	H	-1.411857	3.544489	-1.993790
3	1	H	-1.307715	5.253199	-1.537034
4	1	H	-2.240182	4.123489	-0.539694
5	6	C	-0.092947	3.919391	-0.304948
6	1	H	0.808252	4.033827	-0.923988
7	1	H	-0.018562	4.657542	0.507947
8	6	C	-0.104174	2.493584	0.281332
9	1	H	-1.009684	2.402910	0.907552
10	1	H	0.738154	2.424428	0.990748
11	6	C	-0.040273	1.320949	-0.717364
12	1	H	0.833637	1.489665	-1.378837
13	1	H	-0.903238	1.400272	-1.405917
14	3	Li	-1.100446	-0.419695	0.057324
15	6	C	0.631276	-4.483288	-1.849516
16	1	H	1.384134	-4.516275	-2.644388
17	1	H	-0.357235	-4.459756	-2.322010
18	1	H	0.705026	-5.413683	-1.275779
19	6	C	0.818810	-3.269010	-0.937353
20	1	H	1.821774	-3.298910	-0.487526
21	1	H	0.773622	-2.348567	-1.536337
22	6	C	-0.218096	-3.181930	0.187439
23	1	H	-0.210721	-4.155164	0.713407
24	1	H	-1.214634	-3.115375	-0.282875
25	6	C	0.018296	-1.964077	1.109121
26	1	H	0.970447	-2.143917	1.649655
27	1	H	-0.739374	-1.985614	1.918156
28	3	Li	1.146048	-0.235604	0.285797
29	6	C	4.060254	-0.646982	1.008202
30	8	O	3.031072	0.169526	0.396371
31	6	C	3.632833	1.327461	-0.235853

32	6	C	5.059718	1.376659	0.295717
33	6	C	5.377278	-0.113539	0.457230
34	1	H	4.002398	-0.520859	2.094974
35	1	H	3.861266	-1.689822	0.751275
36	1	H	3.616725	1.178176	-1.321140
37	1	H	3.029427	2.200971	0.019422
38	1	H	5.735848	1.893432	-0.389033
39	1	H	5.086591	1.877596	1.268706
40	1	H	5.590757	-0.562361	-0.518137
41	1	H	6.214826	-0.310430	1.130096
42	6	C	-3.775245	0.733994	-0.428897
43	8	O	-3.033375	-0.468407	-0.087257
44	6	C	-3.861641	-1.333196	0.725164
45	6	C	-4.918885	-0.413121	1.316527
46	6	C	-5.180090	0.531254	0.138028
47	1	H	-3.267610	1.584666	0.036697
48	1	H	-3.755609	0.852286	-1.514867
49	1	H	-4.315173	-2.097297	0.082629
50	1	H	-3.214078	-1.813444	1.461686
51	1	H	-5.808794	-0.956198	1.642778
52	1	H	-4.503634	0.138866	2.165900
53	1	H	-5.822718	0.040333	-0.599439
54	1	H	-5.640465	1.477117	0.431913

E(RMP2) = –793.39165202 Hartree

Table A23. Cartesian coordinates and energies for (*n*-BuLi)$_2$·2THF (chair conformation) found in Table 3.2. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-1.954809	4.128107	-0.998244
2	1	H	-2.043405	3.467560	-1.865051
3	1	H	-2.083255	5.158032	-1.345788
4	1	H	-2.786166	3.898359	-0.321892
5	6	C	-0.610583	3.930814	-0.290371
6	1	H	0.204752	4.203639	-0.973635
7	1	H	-0.551775	4.626664	0.559468
8	6	C	-0.376115	2.483566	0.199775
9	1	H	-1.209299	2.226306	0.874599
10	1	H	0.511616	2.500358	0.851989
11	6	C	-0.207113	1.385947	-0.871497
12	1	H	0.618731	1.695388	-1.541236
13	1	H	-1.093759	1.403166	-1.531907
14	3	Li	-1.062657	-0.524629	-0.267956
15	6	C	1.472182	-4.772590	-1.507535
16	1	H	2.277223	-4.815306	-2.248202
17	1	H	0.535823	-5.021749	-2.018839
18	1	H	1.659889	-5.556759	-0.766336
19	6	C	1.381658	-3.395577	-0.841459
20	1	H	2.339730	-3.162405	-0.356789
21	1	H	1.236914	-2.623880	-1.608978
22	6	C	0.260312	-3.277877	0.199804
23	1	H	0.387718	-4.114835	0.912482

24	1	H	-0.694047	-3.485121	-0.310718
25	6	C	0.206348	-1.888353	0.873121
26	1	H	1.115707	-1.794845	1.502269
27	1	H	-0.609770	-1.900822	1.622138
28	3	Li	1.119475	-0.096859	0.009931
29	6	C	3.999132	-0.331778	0.885901
30	8	O	2.966650	0.406883	0.178169
31	6	C	3.493966	1.674794	-0.295088
32	6	C	4.791004	1.881302	0.480074
33	6	C	5.295920	0.439498	0.642075
34	1	H	3.734787	-0.357287	1.947649
35	1	H	4.014760	-1.352441	0.499803
36	1	H	3.675568	1.596376	-1.372222
37	1	H	2.738415	2.441001	-0.117891
38	1	H	5.492049	2.526987	-0.050718
39	1	H	4.582940	2.325790	1.457523
40	1	H	5.774415	0.099720	-0.280692
41	1	H	6.006054	0.319331	1.461324
42	6	C	-3.832923	0.569048	-0.291306
43	8	O	-2.980418	-0.590948	-0.079541
44	6	C	-3.712525	-1.624357	0.628047
45	6	C	-4.917316	-0.913260	1.235201
46	6	C	-5.228942	0.144810	0.165798
47	1	H	-3.438594	1.393636	0.308679
48	1	H	-3.780802	0.846108	-1.345480
49	1	H	-4.018855	-2.392049	-0.090999
50	1	H	-3.039184	-2.071222	1.360683
51	1	H	-5.748843	-1.593655	1.424411
52	1	H	-4.639237	-0.434502	2.178453
53	1	H	-5.783299	-0.305763	-0.662276
54	1	H	-5.808281	0.986638	0.547467

E(RB3LYP) = –795.98514597 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.475124		
Thermal correction to Energy =		0.489754		
Thermal correction to Enthalpy		0.490372		
Thermal correction to Gibbs Free Energy =		0.438444		
Sum of electronic and zero-point Energies =		-795.510022		
Sum of electronic and thermal Energies =		-795.495392		
Sum of electronic and thermal Enthalpies =		-795.494774		
Sum of electronic and thermal Free Energies =		-795.546702		

Table A24. Cartesian coordinates and energy for $(n\text{-BuLi})_2{\cdot}4\text{THF}$ (boat conformation) found in Table 3.2. Structure was optimised at the RMP2/6-311++G(d,p) level of theory. Energy value is reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	2.043355	3.409995	3.370475
2	1	H	2.971745	3.287996	2.800072
3	1	H	2.309442	3.739962	4.381046
4	1	H	1.465020	4.211637	2.895677

5	6	C	1.243107	2.104060	3.378126
6	1	H	1.821927	1.313049	3.875936
7	1	H	0.322375	2.232467	3.964771
8	6	C	0.863615	1.621379	1.969177
9	1	H	1.798738	1.531987	1.389996
10	1	H	0.312633	2.443682	1.482474
11	6	C	0.054164	0.316425	1.856901
12	1	H	-0.887358	0.444657	2.431393
13	1	H	0.606434	-0.463691	2.425397
14	3	Li	-0.823181	0.530408	-0.158960
15	6	C	3.579778	1.804874	-3.370762
16	1	H	3.486303	2.729480	-2.788856
17	1	H	3.876627	2.076517	-4.390117
18	1	H	4.392202	1.215456	-2.929116
19	6	C	2.267163	1.016152	-3.339090
20	1	H	1.465122	1.605899	-3.805704
21	1	H	2.367326	0.098927	-3.936535
22	6	C	1.829271	0.630881	-1.917240
23	1	H	1.775852	1.562282	-1.327767
24	1	H	2.658910	0.062739	-1.464828
25	6	C	0.520143	-0.164437	-1.764040
26	1	H	0.630447	-1.117693	-2.321166
27	1	H	-0.267370	0.381001	-2.330240
28	3	Li	0.731333	-1.065538	0.259568
29	6	C	3.624377	-0.784691	1.186474
30	8	O	2.586798	-1.608737	0.615476
31	6	C	3.163710	-2.503611	-0.367367
32	6	C	4.641896	-2.124558	-0.464254
33	6	C	4.916465	-1.548090	0.929729
34	1	H	3.635939	0.186939	0.677287
35	1	H	3.383948	-0.636977	2.241763
36	1	H	3.030607	-3.529153	-0.006451
37	1	H	2.621215	-2.378169	-1.309278
38	1	H	5.269873	-2.983294	-0.713669
39	1	H	4.786436	-1.349022	-1.223567
40	1	H	5.033426	-2.353232	1.662669
41	1	H	5.796419	-0.901190	0.964792
42	6	C	-0.514135	3.373677	-1.224952
43	8	O	-1.347995	2.389630	-0.576860
44	6	C	-2.209114	3.046085	0.384578
45	6	C	-1.812291	4.522973	0.369465
46	6	C	-1.257476	4.690287	-1.049954
47	1	H	0.461803	3.406251	-0.724852
48	1	H	-0.378964	3.057552	-2.261540
49	1	H	-3.246014	2.903476	0.058710
50	1	H	-2.066882	2.570606	1.359990
51	1	H	-2.659099	5.177631	0.588984
52	1	H	-1.021333	4.710532	1.103060
53	1	H	-2.073540	4.764589	-1.776468
54	1	H	-0.601195	5.557201	-1.158249
55	6	C	-3.564786	-0.348441	0.890861
56	8	O	-2.635469	-0.274807	-0.207254
57	6	C	-3.412432	-0.235894	-1.410644
58	6	C	-4.517387	-1.251552	-1.152669
59	6	C	-4.860723	-0.973360	0.323687
60	1	H	-3.090572	-0.946782	1.670942
61	1	H	-3.747017	0.659427	1.281490

62	1	H	-3.823308	0.773549	-1.559694
63	1	H	-2.743486	-0.483059	-2.237419
64	1	H	-5.374274	-1.127964	-1.819607
65	1	H	-4.115933	-2.261893	-1.277599
66	1	H	-5.686928	-0.260682	0.394607
67	1	H	-5.148059	-1.880049	0.861507
68	6	C	-0.878857	-3.301339	-0.875582
69	8	O	-0.147271	-2.856978	0.286916
70	6	C	-0.872036	-3.232447	1.483973
71	6	C	-2.168284	-3.891222	1.008063
72	6	C	-1.769176	-4.428423	-0.370835
73	1	H	-1.469682	-2.463687	-1.262472
74	1	H	-0.148704	-3.607432	-1.628391
75	1	H	-0.247880	-3.935621	2.047133
76	1	H	-1.033392	-2.331385	2.082215
77	1	H	-2.511651	-4.666176	1.697975
78	1	H	-2.958592	-3.142708	0.899131
79	1	H	-1.191261	-5.353392	-0.270154
80	1	H	-2.623339	-4.612064	-1.028048

E(RMP2) = –1257.10680648 Hartree

Table A25. Cartesian coordinates and energies for $(n\text{-BuLi})_2\cdot 4\text{THF}$ (boat conformation) found in Table 3.2 and Table 3.6. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	1.873595	3.388106	3.611099
2	1	H	2.834795	3.330610	3.087799
3	1	H	2.077194	3.666307	4.650499
4	1	H	1.302191	4.204104	3.154099
5	6	C	1.112000	2.061103	3.502999
6	1	H	1.686104	1.263405	3.992999
7	1	H	0.163600	2.131999	4.052299
8	6	C	0.811302	1.633302	2.053899
9	1	H	1.773202	1.586806	1.518699
10	1	H	0.270999	2.462999	1.574299
11	6	C	0.033008	0.320898	1.849799
12	1	H	-0.941993	0.417694	2.367399
13	1	H	0.556711	-0.468399	2.427899
14	3	Li	-0.773193	0.543895	-0.191801
15	6	C	3.632303	1.538214	-3.588801
16	1	H	3.608899	2.500613	-3.065101
17	1	H	3.893502	1.734615	-4.634001
18	1	H	4.443605	0.947417	-3.148601
19	6	C	2.289806	0.809008	-3.451801
20	1	H	1.495803	1.402305	-3.925001
21	1	H	2.325410	-0.140892	-4.001701
22	6	C	1.885707	0.520406	-1.993301
23	1	H	1.882703	1.483306	-1.458601
24	1	H	2.708709	-0.045690	-1.532601
25	6	C	0.557310	-0.220699	-1.758901
26	1	H	0.625014	-1.207999	-2.255701
27	1	H	-0.227192	0.309497	-2.338501

28	3	Li	0.717914	-1.074399	0.282799
29	6	C	3.575912	-0.766687	1.229599
30	8	O	2.573716	-1.627391	0.642899
31	6	C	3.195220	-2.561288	-0.276001
32	6	C	4.671218	-2.161382	-0.349001
33	6	C	4.900015	-1.493681	1.016299
34	1	H	3.563308	0.198913	0.712699
35	1	H	3.310012	-0.609288	2.275699
36	1	H	3.063324	-3.569989	0.127599
37	1	H	2.680920	-2.493390	-1.237201
38	1	H	5.322822	-3.018379	-0.526301
39	1	H	4.829215	-1.437581	-1.153201
40	1	H	5.050018	-2.249281	1.792999
41	1	H	5.753812	-0.814078	1.025599
42	6	C	-0.300405	3.387397	-1.212101
43	8	O	-1.205401	2.429493	-0.618801
44	6	C	-2.155604	3.108189	0.238499
45	6	C	-1.728010	4.577991	0.263299
46	6	C	-1.005911	4.733794	-1.084101
47	1	H	0.643395	3.377401	-0.655901
48	1	H	-0.107604	3.071898	-2.238101
49	1	H	-3.153303	2.977985	-0.193301
50	1	H	-2.132402	2.636989	1.223699
51	1	H	-2.576613	5.253387	0.381699
52	1	H	-1.030411	4.755394	1.086599
53	1	H	-1.728611	4.864791	-1.894901
54	1	H	-0.308314	5.572697	-1.104201
55	6	C	-3.560790	-0.262717	0.819899
56	8	O	-2.628990	-0.163913	-0.277801
57	6	C	-3.373990	-0.199916	-1.504601
58	6	C	-4.491986	-1.198121	-1.224101
59	6	C	-4.857187	-0.875022	0.239899
60	1	H	-3.086787	-0.875615	1.586199
61	1	H	-3.735894	0.733883	1.237199
62	1	H	-3.771594	0.798882	-1.731001
63	1	H	-2.685789	-0.494013	-2.297301
64	1	H	-5.336286	-1.092524	-1.907101
65	1	H	-4.103982	-2.216119	-1.310901
66	1	H	-5.671190	-0.148226	0.280199
67	1	H	-5.175184	-1.760123	0.792899
68	6	C	-0.995577	-3.262806	-0.821701
69	8	O	-0.265979	-2.817503	0.343899
70	6	C	-0.980778	-3.194706	1.547599
71	6	C	-2.276975	-3.868511	1.083099
72	6	C	-1.906273	-4.377410	-0.318401
73	1	H	-1.566681	-2.419908	-1.220901
74	1	H	-0.268576	-3.582003	-1.569601
75	1	H	-0.345375	-3.882803	2.113999
76	1	H	-1.146581	-2.294607	2.142799
77	1	H	-2.594771	-4.661713	1.761499
78	1	H	-3.085778	-3.137615	1.014099
79	1	H	-1.355469	-5.320107	-0.251601
80	1	H	-2.773272	-4.530313	-0.963801

E(RB3LYP) = –1261.08161574 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.712502		
Thermal correction to Energy =		0.733003		
Thermal correction to Enthalpy		0.733621		
Thermal correction to Gibbs Free Energy =		0.670255		
Sum of electronic and zero-point Energies =		-1260.369113		
Sum of electronic and thermal Energies =		-1260.348612		
Sum of electronic and thermal Enthalpies =		-1260.347994		
Sum of electronic and thermal Free Energies =		-1260.411361		

Thermochemistry:	Temperature:	185.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.712502		
Thermal correction to Energy =		0.731379		
Thermal correction to Enthalpy		0.731965		
Thermal correction to Gibbs Free Energy =		0.673458		
Sum of electronic and zero-point Energies =		-1260.369113		
Sum of electronic and thermal Energies =		-1260.350237		
Sum of electronic and thermal Enthalpies =		-1260.349650		
Sum of electronic and thermal Free Energies =		-1260.408157		

Table A26. Cartesian coordinates and energy for (n-BuLi)$_2$·4THF (chair conformation) found in Table 3.2. Structure was optimised at the RMP2/6-311++G(d,p) level of theory. Energy value is reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	4.436540	-1.205311	-3.330036
2	1	H	5.083026	-0.859856	-4.144498
3	1	H	4.013835	-2.173369	-3.623177
4	1	H	5.065285	-1.370670	-2.447368
5	6	C	3.320169	-0.205597	-3.014563
6	1	H	3.755622	0.766031	-2.740661
7	1	H	2.709367	-0.030503	-3.911347
8	6	C	2.396110	-0.663115	-1.874923
9	1	H	3.033752	-0.865731	-0.996617
10	1	H	1.988626	-1.648910	-2.157918
11	6	C	1.242304	0.283008	-1.498006
12	1	H	0.619050	0.399559	-2.410872
13	1	H	1.678794	1.294075	-1.351587
14	3	Li	0.972255	-0.248142	0.633534
15	6	C	-4.165990	1.148934	3.373150
16	1	H	-3.688093	2.085973	3.682106
17	1	H	-4.799037	0.805666	4.199037
18	1	H	-4.816665	1.373283	2.519877
19	6	C	-3.109795	0.110490	2.983859
20	1	H	-2.476069	-0.122496	3.851428
21	1	H	-3.599725	-0.830611	2.695723
22	6	C	-2.208061	0.564874	1.825593
23	1	H	-1.746996	1.522290	2.124333
24	1	H	-2.864592	0.829030	0.979564
25	6	C	-1.117079	-0.419708	1.369320
26	1	H	-1.614998	-1.394098	1.170017
27	1	H	-0.489920	-0.632315	2.262066

28	3	Li	-0.839665	0.144166	-0.762553
29	6	C	-1.408388	-2.193097	-2.431649
30	8	O	-1.962417	-0.941702	-1.970416
31	6	C	-3.323469	-1.158491	-1.516881
32	6	C	-3.631589	-2.633752	-1.784348
33	6	C	-2.235560	-3.266314	-1.738636
34	1	H	-1.520280	-2.255577	-3.522043
35	1	H	-0.346312	-2.191959	-2.175801
36	1	H	-3.359345	-0.925977	-0.447612
37	1	H	-3.981033	-0.473524	-2.059756
38	1	H	-4.321037	-3.046517	-1.044175
39	1	H	-4.066915	-2.760451	-2.780933
40	1	H	-1.905613	-3.384532	-0.701129
41	1	H	-2.179435	-4.232611	-2.246454
42	6	C	1.915266	-2.304239	2.549393
43	8	O	1.787885	-1.999694	1.141988
44	6	C	1.107951	-3.092434	0.475140
45	6	C	0.982561	-4.208375	1.510273
46	6	C	0.905629	-3.412810	2.818094
47	1	H	2.939848	-2.646318	2.744147
48	1	H	1.730632	-1.382675	3.105850
49	1	H	1.692699	-3.371688	-0.405071
50	1	H	0.124163	-2.727627	0.161950
51	1	H	0.105939	-4.835880	1.329577
52	1	H	1.877202	-4.840196	1.503689
53	1	H	-0.093141	-2.983179	2.942810
54	1	H	1.161184	-4.002905	3.702071
55	6	C	3.183395	1.649675	1.262899
56	8	O	2.037817	0.960864	1.783797
57	6	C	1.445384	1.843123	2.755514
58	6	C	1.759728	3.282949	2.287812
59	6	C	2.697570	3.083051	1.076093
60	1	H	4.004139	1.596272	1.992555
61	1	H	3.475469	1.147931	0.338434
62	1	H	0.379940	1.609907	2.787809
63	1	H	1.893755	1.640116	3.736186
64	1	H	0.851422	3.824581	2.012666
65	1	H	2.258647	3.841802	3.083901
66	1	H	2.140838	3.152356	0.138105
67	1	H	3.518674	3.804249	1.051923
68	6	C	-0.930275	2.935929	-0.401852
69	8	O	-1.652101	1.914095	-1.128708
70	6	C	-1.827937	2.331661	-2.503770
71	6	C	-1.396841	3.795766	-2.551977
72	6	C	-0.313406	3.832157	-1.467975
73	1	H	-1.640368	3.490147	0.225098
74	1	H	-0.201354	2.427041	0.233575
75	1	H	-1.191861	1.705573	-3.139061
76	1	H	-2.875155	2.173183	-2.774758
77	1	H	-1.034003	4.085151	-3.541207
78	1	H	-2.231064	4.448864	-2.274477
79	1	H	0.611015	3.382107	-1.843971
80	1	H	-0.102461	4.838163	-1.095384

E(RMP2) = –1257.10874668 Hartree

Table A27. Cartesian coordinates and energies for $(n\text{-BuLi})_2\cdot$4THF (chair conformation) found in Table 3.2. and Table 3.6. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-2.506493	-2.749199	3.825000
2	1	H	-2.781492	-2.785210	4.884300
3	1	H	-1.937856	-3.657975	3.597800
4	1	H	-3.431892	-2.788137	3.239300
5	6	C	-1.695244	-1.494665	3.478100
6	1	H	-2.273081	-0.597889	3.738400
7	1	H	-0.787146	-1.455928	4.094300
8	6	C	-1.290048	-1.407049	1.994500
9	1	H	-2.209344	-1.500387	1.395600
10	1	H	-0.720211	-2.318526	1.754700
11	6	C	-0.496599	-0.164316	1.558100
12	1	H	0.424200	-0.131979	2.174100
13	1	H	-1.061935	0.726060	1.899800
14	3	Li	-1.086709	0.078359	-0.560900
15	6	C	1.199406	4.600453	-3.306300
16	1	H	0.404784	5.150420	-2.789400
17	1	H	1.297889	5.025557	-4.310800
18	1	H	2.134398	4.796491	-2.769400
19	6	C	0.891768	3.098040	-3.339800
20	1	H	-0.031725	2.922403	-3.907600
21	1	H	1.685989	2.569873	-3.884100
22	6	C	0.741594	2.459834	-1.945600
23	1	H	-0.039829	3.022802	-1.409300
24	1	H	1.666585	2.662672	-1.385100
25	6	C	0.425555	0.954121	-1.898600
26	1	H	1.233377	0.422054	-2.438400
27	1	H	-0.462938	0.789785	-2.540300
28	3	Li	1.111984	0.246149	0.083000
29	6	C	2.452690	-2.334296	1.000400
30	8	O	2.330048	-1.314601	-0.014600
31	6	C	2.987466	-1.744174	-1.233500
32	6	C	3.592522	-3.119749	-0.929500
33	6	C	2.722443	-3.624385	0.233200
34	1	H	3.289880	-2.084162	1.663500
35	1	H	1.528490	-2.334834	1.578300
36	1	H	2.231067	-1.786505	-2.021000
37	1	H	3.734235	-0.996743	-1.510700
38	1	H	3.571949	-3.777850	-1.799600
39	1	H	4.631518	-3.018407	-0.604700
40	1	H	1.785160	-4.046023	-0.140000
41	1	H	3.218974	-4.378964	0.845200
42	6	C	-2.117539	-1.627283	-2.733000
43	8	O	-1.724738	-1.662367	-1.345800
44	6	C	-0.775893	-2.745828	-1.150600
45	6	C	-0.431971	-3.285614	-2.550100
46	6	C	-0.906617	-2.161733	-3.487500
47	1	H	-2.997613	-2.267019	-2.880700
48	1	H	-2.380781	-0.596894	-2.973700
49	1	H	-1.232662	-3.501747	-0.507300
50	1	H	0.085389	-2.320793	-0.635600

51	1	H	0.631638	-3.506270	-2.653200
52	1	H	-0.985534	-4.206236	-2.753000
53	1	H	-0.152049	-1.375302	-3.564100
54	1	H	-1.154703	-2.516043	-4.489600
55	6	C	-3.988023	0.420141	-0.191000
56	8	O	-2.796250	1.091489	-0.651700
57	6	C	-2.727704	2.405092	-0.036400
58	6	C	-3.827706	2.444947	1.041300
59	6	C	-4.212145	0.964532	1.213900
60	1	H	-4.825933	0.667006	-0.856000
61	1	H	-3.793979	-0.651051	-0.239000
62	1	H	-1.726008	2.509533	0.383100
63	1	H	-2.867335	3.164987	-0.809700
64	1	H	-3.473124	2.900262	1.967200
65	1	H	-4.687129	3.020812	0.688800
66	1	H	-3.533925	0.468659	1.911400
67	1	H	-5.237939	0.827490	1.560800
68	6	C	1.525882	2.750466	1.530900
69	8	O	2.246729	1.604696	1.007800
70	6	C	3.229147	1.158836	1.972100
71	6	C	3.358700	2.296141	2.982400
72	6	C	1.930377	2.860683	3.000100
73	1	H	1.824246	3.633379	0.957100
74	1	H	0.459989	2.572623	1.385000
75	1	H	2.863984	0.243821	2.450800
76	1	H	4.152256	0.931574	1.435900
77	1	H	3.698915	1.946655	3.958600
78	1	H	4.063470	3.050670	2.620600
79	1	H	1.282303	2.232256	3.617300
80	1	H	1.873935	3.885781	3.369800

E(RB3LYP) = –1261.08255541 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.712931
Thermal correction to Energy = 0.733294
Thermal correction to Enthalpy 0.733912
Thermal correction to Gibbs Free Energy = 0.671276
Sum of electronic and zero-point Energies = -1260.369625
Sum of electronic and thermal Energies = -1260.349261
Sum of electronic and thermal Enthalpies = -1260.348643
Sum of electronic and thermal Free Energies = -1260.411279

Thermochemistry: Temperature: 185.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.712931
Thermal correction to Energy = 0.731673
Thermal correction to Enthalpy 0.732260
Thermal correction to Gibbs Free Energy = 0.674443
Sum of electronic and zero-point Energies = -1260.369624
Sum of electronic and thermal Energies = -1260.350882
Sum of electronic and thermal Enthalpies = -1260.350296
Sum of electronic and thermal Free Energies = -1260.408112

Table A28. Cartesian coordinates and energies for the LEC of (*n*-BuLi)$_4$·found in Figure 3.4. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	1.386310	-0.559687	-0.915304
2	3	Li	0.797584	1.112104	0.728396
3	3	Li	-0.916094	-0.285623	-0.255104
4	3	Li	0.645721	-1.248198	1.325196
5	6	C	0.167282	1.263194	-1.417704
6	6	C	0.116258	2.772193	-1.084804
7	6	C	-0.129957	3.720790	-2.271004
8	6	C	-0.175580	5.201689	-1.879904
9	6	C	2.588605	-0.208968	0.929096
10	6	C	3.741910	-0.537350	-0.048504
11	6	C	5.182307	-0.361027	0.480196
12	6	C	5.541422	-1.311122	1.626396
13	6	C	-0.002863	-2.281008	-0.540904
14	6	C	-1.423757	-2.646131	-1.029204
15	6	C	-1.634134	-4.102034	-1.481304
16	6	C	-3.064530	-4.405656	-1.939504
17	6	C	-0.900103	0.290978	1.898496
18	6	C	-2.377707	0.560754	1.528596
19	6	C	-3.297315	1.029840	2.669596
20	6	C	-4.742819	1.282417	2.227596
21	1	H	1.056553	3.096608	-0.604404
22	1	H	-0.671345	2.964481	-0.337904
23	1	H	-1.072552	3.434875	-2.754404
24	1	H	0.657146	3.557702	-3.017904
25	1	H	0.767415	5.514904	-1.418904
26	1	H	-0.351690	5.845686	-2.747004
27	1	H	-0.975283	5.391676	-1.156004
28	1	H	2.710715	-0.875966	1.804696
29	1	H	2.824389	0.788336	1.356896
30	1	H	3.662700	0.090449	-0.952304
31	1	H	3.649226	-1.577651	-0.402504
32	1	H	5.304791	0.677275	0.814396
33	1	H	4.894819	-1.150932	2.493196
34	1	H	5.428638	-2.356023	1.316096
35	1	H	0.254349	-3.025504	0.240896
36	1	H	0.688741	-2.559798	-1.361204
37	1	H	-1.715967	-1.996635	-1.871404
38	1	H	-2.162360	-2.443042	-0.235504
39	1	H	-1.361124	-4.766330	-0.651704
40	1	H	-0.928231	-4.321223	-2.292204
41	1	H	-3.781933	-4.217367	-1.133404
42	1	H	-3.348140	-3.772361	-2.787004
43	1	H	-3.179513	-5.448658	-2.250304
44	1	H	-0.542517	1.201283	2.422196
45	1	H	-2.837293	-0.347653	1.101996
46	1	H	-2.438419	1.322354	0.732196
47	1	H	-2.874829	1.945447	3.101796
48	1	H	-3.276703	0.277240	3.467496
49	1	H	-5.369624	1.620508	3.058396
50	1	H	-4.784631	2.048317	1.445596

51	1	H	-5.193404	0.371110	1.819796
52	1	H	-0.913291	-0.460723	2.712896
53	1	H	-0.781215	1.035279	-1.947204
54	1	H	0.915483	1.148306	-2.228304
55	1	H	5.894009	-0.509316	-0.343304
56	1	H	6.576420	-1.169805	1.951996

E(UB3LYP) = –661.81565272 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.485819	
Thermal correction to Energy =	0.500357	
Thermal correction to Enthalpy	0.500975	
Thermal correction to Gibbs Free Energy =	0.452300	
Sum of electronic and zero-point Energies =	-661.329833	
Sum of electronic and thermal Energies =	-661.315296	
Sum of electronic and thermal Enthalpies =	-661.314678	
Sum of electronic and thermal Free Energies =	-661.363352	

Table A29. Cartesian coordinates and energies for the LEC of (*n*-BuLi)$_4$·4THF·found in Figure 3.4 and Table 3.6. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	-0.699727	-1.122035	-0.850023
2	3	Li	0.982340	-0.870070	0.891373
3	3	Li	0.810320	0.748586	-0.975844
4	3	Li	-0.869359	0.680055	0.809780
5	8	O	-1.732444	-2.259277	-2.036073
6	8	O	1.938514	-1.811561	2.359858
7	8	O	1.916794	1.862543	-2.175502
8	8	O	-1.943348	2.005356	1.799481
9	6	C	1.445796	-1.373307	-1.282309
10	6	C	1.594622	-2.905749	-1.229645
11	6	C	2.432556	-3.544834	-2.351687
12	6	C	2.536457	-5.070854	-2.250543
13	6	C	-1.183288	-1.533209	1.268511
14	6	C	-2.619757	-1.238122	1.747377
15	6	C	-3.394467	-2.422511	2.351038
16	6	C	-4.812675	-2.059700	2.806992
17	6	C	-1.379481	0.960837	-1.373128
18	6	C	-1.414700	2.494131	-1.523235
19	6	C	-2.588734	3.078642	-2.328760
20	6	C	-2.555745	4.607328	-2.439919
21	6	C	1.282715	1.310997	1.153870
22	6	C	2.820239	1.211645	1.079526
23	6	C	3.614748	2.284920	1.843616
24	6	C	5.134265	2.100918	1.754088
25	6	C	-3.171710	-2.370944	-1.892662
26	6	C	-3.727508	-2.374705	-3.315488
27	6	C	-2.584996	-3.029623	-4.106249
28	6	C	-1.352915	-2.442900	-3.422343
29	6	C	1.917439	-1.157308	3.654570

30	6	C	2.158291	-2.264966	4.675526
31	6	C	1.469987	-3.463094	4.005969
32	6	C	1.811998	-3.249108	2.532649
33	6	C	2.341203	3.199110	-1.829377
34	6	C	3.871903	3.234711	-2.039503
35	6	C	4.194474	1.876289	-2.709665
36	6	C	2.826717	1.391704	-3.186825
37	6	C	-3.345564	2.229353	1.498888
38	6	C	-3.584103	3.717363	1.739773
39	6	C	-2.588908	4.020638	2.869340
40	6	C	-1.388861	3.165859	2.469121
41	1	H	0.605011	-3.388784	-1.237540
42	1	H	2.044898	-3.202980	-0.272340
43	1	H	3.436315	-3.100707	-2.337663
44	1	H	1.994140	-3.267493	-3.319463
45	1	H	3.134914	-5.497629	-3.061902
46	1	H	2.998807	-5.369344	-1.303261
47	1	H	1.543915	-5.533335	-2.289897
48	1	H	-0.616124	-1.848440	2.161536
49	1	H	-1.236440	-2.467328	0.671991
50	1	H	-3.229518	-0.836666	0.921999
51	1	H	-2.601677	-0.433179	2.495745
52	1	H	-3.439542	-3.228746	1.607055
53	1	H	-5.405459	-1.676028	1.969042
54	1	H	-5.344963	-2.920374	3.224740
55	1	H	-2.379760	0.644254	-1.015493
56	1	H	-1.339538	0.536281	-2.394660
57	1	H	-0.485069	2.839926	-1.996223
58	1	H	-1.423481	2.973890	-0.533455
59	1	H	-3.530981	2.762953	-1.861573
60	1	H	-2.585349	2.633014	-3.331952
61	1	H	-1.636749	4.943392	-2.932649
62	1	H	-3.402961	4.998022	-3.012738
63	1	H	-2.582676	5.072494	-1.448167
64	1	H	1.007429	1.321511	2.224661
65	1	H	3.148473	1.239275	0.031998
66	1	H	3.157926	0.229823	1.441947
67	1	H	3.301795	2.274615	2.895770
68	1	H	3.336087	3.273574	1.455490
69	1	H	5.677538	2.884455	2.292019
70	1	H	5.434911	1.135891	2.176452
71	1	H	5.470829	2.117864	0.711738
72	1	H	-3.521819	-1.532164	-1.289303
73	1	H	-3.391399	-3.304460	-1.364516
74	1	H	-3.888477	-1.349640	-3.660941
75	1	H	-4.671716	-2.916395	-3.389387
76	1	H	-2.612686	-2.803525	-5.173266
77	1	H	-2.608800	-4.116215	-3.982525
78	1	H	-0.476554	-3.091565	-3.447936
79	1	H	-1.085111	-1.467532	-3.843421
80	1	H	0.935957	-0.690921	3.793434
81	1	H	2.680501	-0.378291	3.651434
82	1	H	1.744322	-2.020595	5.655114
83	1	H	3.229721	-2.453447	4.789988
84	1	H	0.387539	-3.408271	4.152037
85	1	H	1.820281	-4.428074	4.375672
86	1	H	2.768364	-3.708973	2.264131

87	1	H	1.038562	-3.609485	1.853202
88	1	H	2.036213	3.380080	-0.799947
89	1	H	1.827243	3.911346	-2.483866
90	1	H	4.400576	3.348584	-1.092751
91	1	H	4.150884	4.072411	-2.681109
92	1	H	4.596032	1.172682	-1.977383
93	1	H	4.911606	1.965618	-3.527295
94	1	H	2.554708	1.837324	-4.152798
95	1	H	2.725972	0.309015	-3.244803
96	1	H	-3.945037	1.606823	2.170294
97	1	H	-3.525726	1.916745	0.470152
98	1	H	-4.620414	3.932474	2.004826
99	1	H	-3.329993	4.291410	0.844369
100	1	H	-2.991821	3.689712	3.830977
101	1	H	-2.333125	5.078366	2.949144
102	1	H	-0.734760	3.692605	1.767290
103	1	H	-0.788422	2.817619	3.310580
104	1	H	1.003129	2.327423	0.819151
105	1	H	2.461391	-0.943562	-1.201342
106	1	H	1.143662	-1.122899	-2.319805
107	1	H	-2.822001	-2.823252	3.197650
108	1	H	-4.788316	-1.278333	3.574685

E(UB3LYP) = –1592.01793148 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.957421	
Thermal correction to Energy =	0.985509	
Thermal correction to Enthalpy	0.986127	
Thermal correction to Gibbs Free Energy =	0.905635	
Sum of electronic and zero-point Energies =	-1591.060510	
Sum of electronic and thermal Energies =	-1591.032423	
Sum of electronic and thermal Enthalpies =	-1591.031805	
Sum of electronic and thermal Free Energies =	-1591.112296	

Thermochemistry:	Temperature: 185.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.957421	
Thermal correction to Energy =	0.983219	
Thermal correction to Enthalpy	0.983806	
Thermal correction to Gibbs Free Energy =	0.909699	
Sum of electronic and zero-point Energies =	-1591.060510	
Sum of electronic and thermal Energies =	-1591.034712	
Sum of electronic and thermal Enthalpies =	-1591.034126	
Sum of electronic and thermal Free Energies =	-1591.108233	

Table A30. Cartesian coordinates and energies for the STQN output found in Figure 3.5. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	1.089893	-1.327201	1.578507
2	3	Li	-0.439307	-2.121400	0.104507
3	3	Li	-0.337904	1.642900	-0.039793
4	3	Li	1.005895	1.020299	-1.739493
5	6	C	-1.062206	-1.021899	1.885007
6	6	C	-2.453007	-1.373198	1.313307
7	6	C	-3.674106	-0.755897	2.019507
8	6	C	-5.015907	-1.194896	1.423007
9	6	C	1.692492	-2.369501	-0.250693
10	6	C	2.270791	-3.790702	-0.084493
11	6	C	3.467891	-4.181203	-0.980693
12	6	C	4.744992	-3.388804	-0.683593
13	6	C	1.809796	1.852998	0.127907
14	6	C	2.452497	3.251498	0.029107
15	6	C	3.667897	3.516797	0.936807
16	6	C	4.260799	4.922596	0.785907
17	6	C	-1.173605	0.752701	-1.835093
18	6	C	-2.485404	1.378502	-1.310993
19	6	C	-3.794205	0.885903	-1.955393
20	6	C	-5.049304	1.571204	-1.403893
21	1	H	-2.594308	-2.467698	1.318607
22	1	H	-2.525906	-1.074298	0.253307
23	1	H	-3.585905	0.337003	1.970307
24	1	H	-3.634006	-1.018597	3.083907
25	1	H	-5.144507	-2.279596	1.507407
26	1	H	-5.862906	-0.719195	1.927307
27	1	H	-5.074506	-0.937596	0.360907
28	1	H	2.518493	-1.642202	-0.123793
29	1	H	1.425493	-2.244101	-1.320893
30	1	H	1.475891	-4.531001	-0.259193
31	1	H	2.578091	-3.951302	0.962007
32	1	H	3.182491	-4.032403	-2.030793
33	1	H	4.586792	-2.316004	-0.825393
34	1	H	5.063491	-3.542004	0.354107
35	1	H	2.610395	1.104798	-0.047493
36	1	H	1.552696	1.683899	1.195807
37	1	H	1.700398	4.027099	0.244707
38	1	H	2.765197	3.447398	-1.009093
39	1	H	4.438097	2.765196	0.719607
40	1	H	3.368897	3.351497	1.980407
41	1	H	4.591399	5.099596	-0.243593
42	1	H	3.516999	5.689797	1.027507
43	1	H	5.122799	5.077096	1.442807
44	1	H	-1.314506	-0.344999	-1.844593
45	1	H	-2.449103	2.473802	-1.429793
46	1	H	-2.600005	1.211402	-0.223593
47	1	H	-3.866206	-0.198597	-1.804693
48	1	H	-3.730005	1.040203	-3.039793
49	1	H	-5.963105	1.181805	-1.863593
50	1	H	-5.133004	1.422904	-0.322393

51	1	H	-5.018103	2.650704	-1.587293
52	1	H	-1.102605	1.014301	-2.908893
53	1	H	-1.027405	0.079101	2.001907
54	1	H	-1.036607	-1.390999	2.928207
55	1	H	3.681690	-5.253603	-0.865893
56	1	H	5.571191	-3.693805	-1.333493

E(UB3LYP) = –661.789054821 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.481956	
Thermal correction to Energy =	0.496876	
Thermal correction to Enthalpy	0.497494	
Thermal correction to Gibbs Free Energy =	0.448228	
Sum of electronic and zero-point Energies =	-661.307099	
Sum of electronic and thermal Energies =	-661.292179	
Sum of electronic and thermal Enthalpies =	-661.291561	
Sum of electronic and thermal Free Energies =	-661.340826	

Appendices

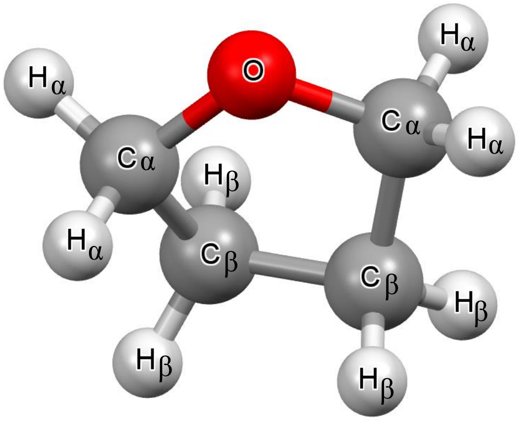
Appendix B:

Supporting Information for Chapter 4

Table B1. Computed isotropic shielding constants (σ_{ref}) for reference molecules; THF (A) and $LiBr{\cdot}6D_2O$ (B)

Structure

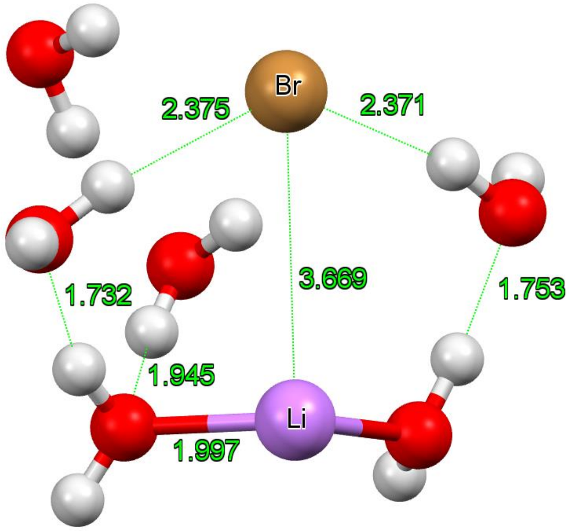
A



	Chemical Shifts (ppm)			
	$^{13}C_{\alpha}$	$^{1}H_{\alpha}$	$^{13}C_{\beta}$	$^{1}H_{\beta}$
	110.07	27.85	152.61	30.03
	110.07	27.85	152.61	30.03
		28.17		30.11
		28.17		30.11
Average (σ_{ref}):	110.07	28.01	152.61	30.07

Structure

B



	Chemical Shifts (ppm)
	^{7}Li
(σ_{ref}):	92.94

Table B2. Cartesian coordinates and energies for the computed reference molecule $LiBr \cdot 6D_2O$ found in Table B1. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

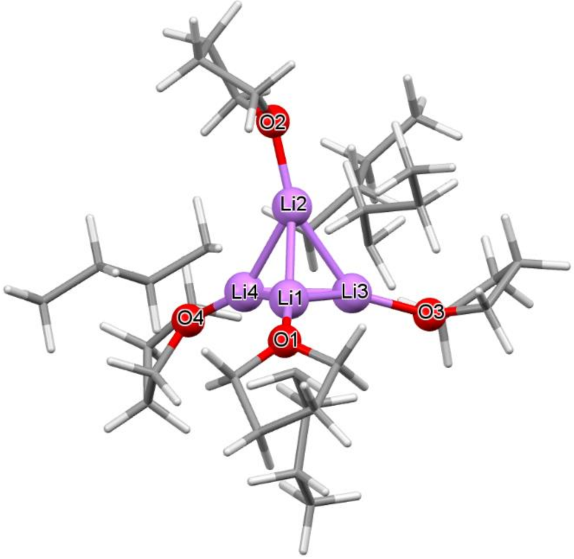
Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	1.436569	1.693043	-1.209030
2	35	Br	-0.436813	-1.406474	-0.624740
3	8	O	2.723475	-1.477691	0.422512
4	1	D	2.776677	-1.803491	1.328473
5	1	D	1.795458	-1.618158	0.147455
6	8	O	-2.144019	1.390000	-1.268275
7	1	D	-2.390883	1.441102	-2.198983
8	1	D	-1.749420	0.502143	-1.149627
9	8	O	0.075853	0.954746	1.882316
10	1	D	0.249360	0.226327	1.263925
11	1	D	0.051415	1.734637	1.301147
12	8	O	-0.019288	2.758079	-0.351872
13	1	D	-0.879377	2.437818	-0.719004
14	1	D	-0.050439	3.720647	-0.331501
15	8	O	-2.487794	-0.290851	2.110281
16	1	D	-2.271655	-0.841044	1.344430
17	1	D	-1.696808	0.273438	2.189644
18	8	O	2.974124	1.183075	-0.110596
19	1	D	3.190464	1.696594	0.674730
20	1	D	2.975142	0.238582	0.167373

E(RB3LYP) = –3040.69476357 Hartree

Thermochemistry:	Temperature: 273.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.109976	
Thermal correction to Energy =	0.129003	
Thermal correction to Enthalpy	0.129868	
Thermal correction to Gibbs Free Energy =	0.064836	
Sum of electronic and zero-point Energies =	-3040.584788	
Sum of electronic and thermal Energies =	-3040.565760	
Sum of electronic and thermal Enthalpies =	-3040.564895	
Sum of electronic and thermal Free Energies =	-3040.629928	

Table B3. Computed isotropic shielding constants (σ_i) for the tetra-solvated *n*-BuLi tetramer $[n\text{-BuLi}]_4\cdot 4\text{THF}$.

Structure



Chemical Shifts (ppm)

	$^{1}H_{\alpha}$	$^{1}H_{\beta}$	$^{1}H_{\gamma}$	$^{1}H_{\delta}$
^{1}H :	32.49	30.35	30.66	31.10
	32.63	30.37	30.69	30.84
	32.70	30.49	30.72	31.09
	32.81	30.73	30.73	31.13
	32.82	30.87	30.77	30.82
	32.90	30.58	30.73	31.06
	33.02	30.34	30.69	30.86
	33.06	30.53	30.74	31.13
				31.15
				30.82
				31.13
				31.08
Average (σ_i):	32.80	30.53	30.72	31.02
	$^{13}C_{\alpha}$	$^{13}C_{\beta}$	$^{13}C_{\gamma}$	$^{13}C_{\delta}$
^{13}C :	169.33	141.52	141.71	166.62
	171.54	144.69	141.30	166.98
	172.91	145.75	142.15	167.04
	174.30	146.63	142.06	167.32
Average (σ_i):	172.02	144.65	141.80	166.99
^{7}Li :	87.75			
	87.76			
	88.36			
	88.38			
Average (σ_i):	88.06			

Table B4. Computed isotropic shielding constants (σ_i) for the tetra-solvated *n*-BuLi dimer $[n\text{-BuLi}]_2\cdot 4\text{THF}$.

Structure

A: Boat Conformation

Chemical Shifts (ppm)

	$^{1}H_{\alpha}$	$^{1}H_{\beta}$	$^{1}H_{\gamma}$	$^{1}H_{\delta}$
^{1}H :	32.59	30.50	30.89	31.17
	32.66	30.51	30.91	30.92
	32.86	30.71	30.95	31.16
	32.99	30.72	30.96	31.16
				30.90
				31.12
Average (σ_i):	32.78	30.61	30.93	31.07
	$^{13}C_{\alpha}$	$^{13}C_{\beta}$	$^{13}C_{\gamma}$	$^{13}C_{\delta}$
^{13}C :	169.54	141.37	139.38	167.04
	169.23	141.71	139.50	167.07
Average (σ_i):	169.39	141.54	139.44	167.06
^{7}Li :	88.64			
	88.65			
Average (σ_i):	88.64			

Structure

B: Chair Conformation

Chemical Shifts (ppm)

	$^{1}H_{\alpha}$	$^{1}H_{\beta}$	$^{1}H_{\gamma}$	$^{1}H_{\delta}$
^{1}H :	32.75	30.46	30.83	30.89
	32.85	30.47	30.86	31.18
	33.13	30.49	30.91	31.15
	33.14	30.52	30.91	31.17
				31.16
				30.90
Average (σ_i):	32.97	30.49	30.88	31.08
	$^{13}C_{\alpha}$	$^{13}C_{\beta}$	$^{13}C_{\gamma}$	$^{13}C_{\delta}$
^{13}C :	168.10	139.84	139.74	167.41
	167.37	140.86	140.01	167.59
Average (σ_i):	167.73	140.35	139.88	167.50
^{7}Li :	88.85			
	89.02			
Average (σ_i):	88.94			

Table B5. Computed isotropic shielding constants (σ_i) for the di-solvated *n*-BuLi dimer $[n\text{-BuLi}]_2\cdot 2\text{THF}$.

Structure

A: Boat Conformation

Chemical Shifts (ppm)

	$^1H_\alpha$	$^1H_\beta$	$^1H_\gamma$	$^1H_\delta$
^{1}H :	32.78	30.70	30.75	30.87
	32.80	30.70	30.78	30.89
	33.03	30.73	30.85	31.11
	33.05	30.74	30.85	31.12
				31.16
				31.16
Average (σ_i):	32.92	30.72	30.81	31.05

	$^{13}C_\alpha$	$^{13}C_\beta$	$^{13}C_\gamma$	$^{13}C_\delta$
^{13}C :	175.18	144.05	141.26	167.21
	174.93	144.19	141.41	167.25
Average (σ_i):	175.05	144.12	141.34	167.23

^{7}Li :	88.16
	88.23
Average (σ_i):	88.20

Structure

B: Chair Conformation

Chemical Shifts (ppm)

	$^1H_\alpha$	$^1H_\beta$	$^1H_\gamma$	$^1H_\delta$
^{1}H :	32.38	30.83	31.19	30.33
	32.49	30.17	30.19	31.15
	32.81	29.59	30.68	31.69
	33.50	30.49	30.69	30.86
				31.17
				31.05
Average (σ_i):	32.80	30.27	30.69	31.04

	$^{13}C_\alpha$	$^{13}C_\beta$	$^{13}C_\gamma$	$^{13}C_\delta$
^{13}C :	179.29	143.19	147.26	166.56
	179.21	146.44	147.47	170.94
Average (σ_i):	179.25	144.82	147.36	168.75

^{7}Li :	87.58
	87.85
Average (σ_i):	87.72

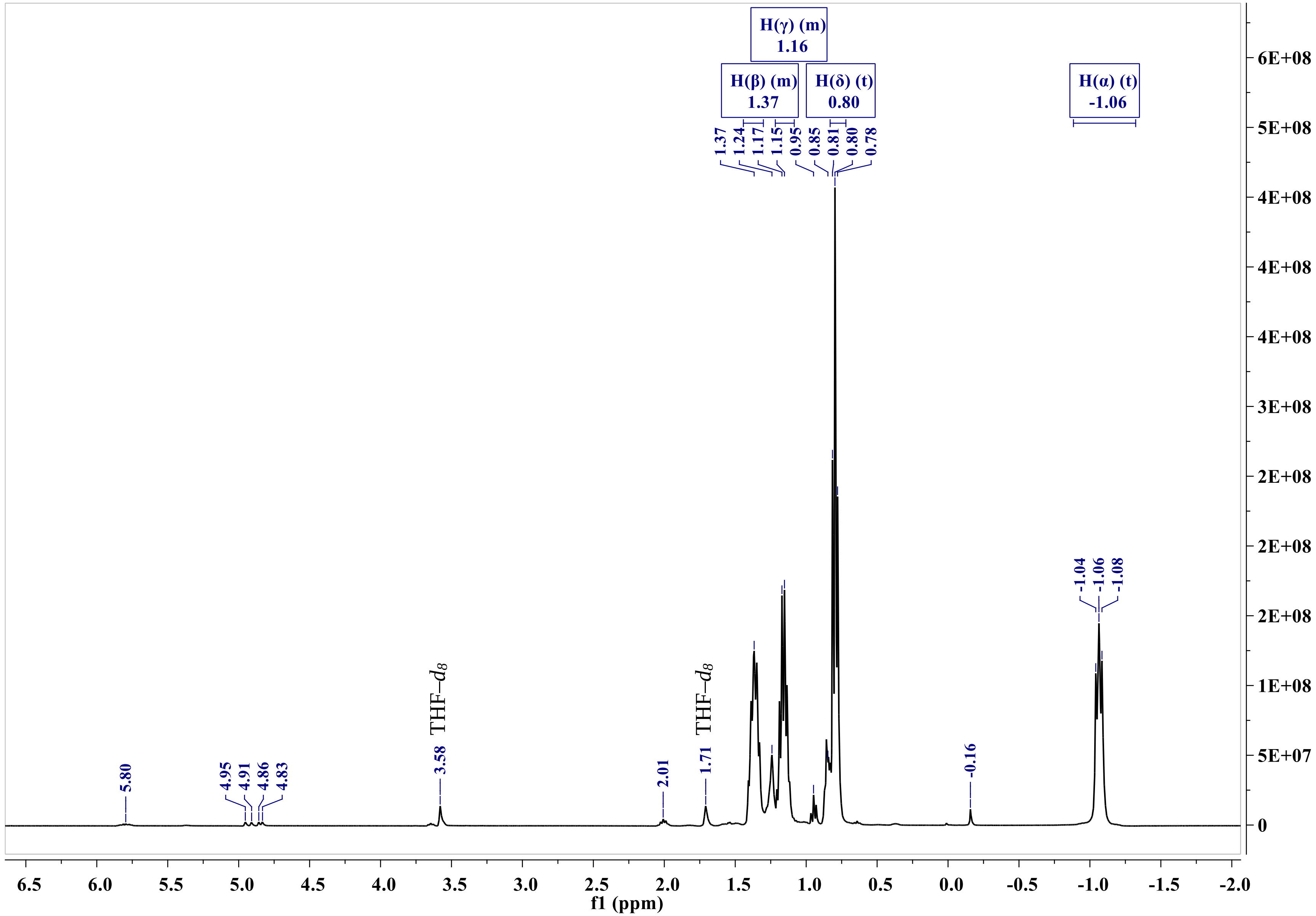


Figure B1. 1-Dimensional experimental ^{1}H NMR spectrum of *n*-BuLi in THF-d_8 at –263.15 Kelvin.

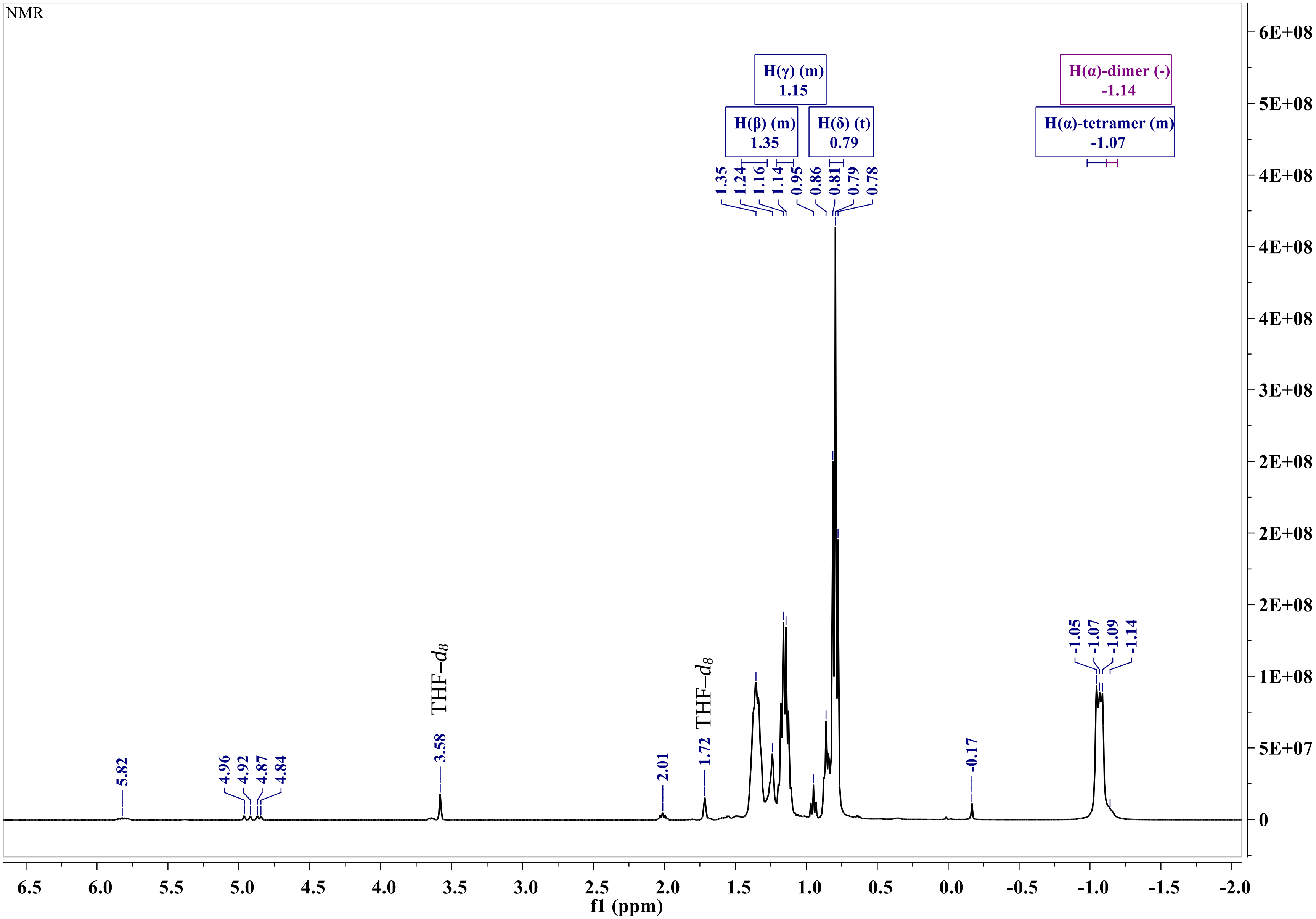


Figure B2. 1-Dimensional experimental ^{1}H NMR spectrum of *n*-BuLi in THF-d_8 at –233.15 Kelvin.

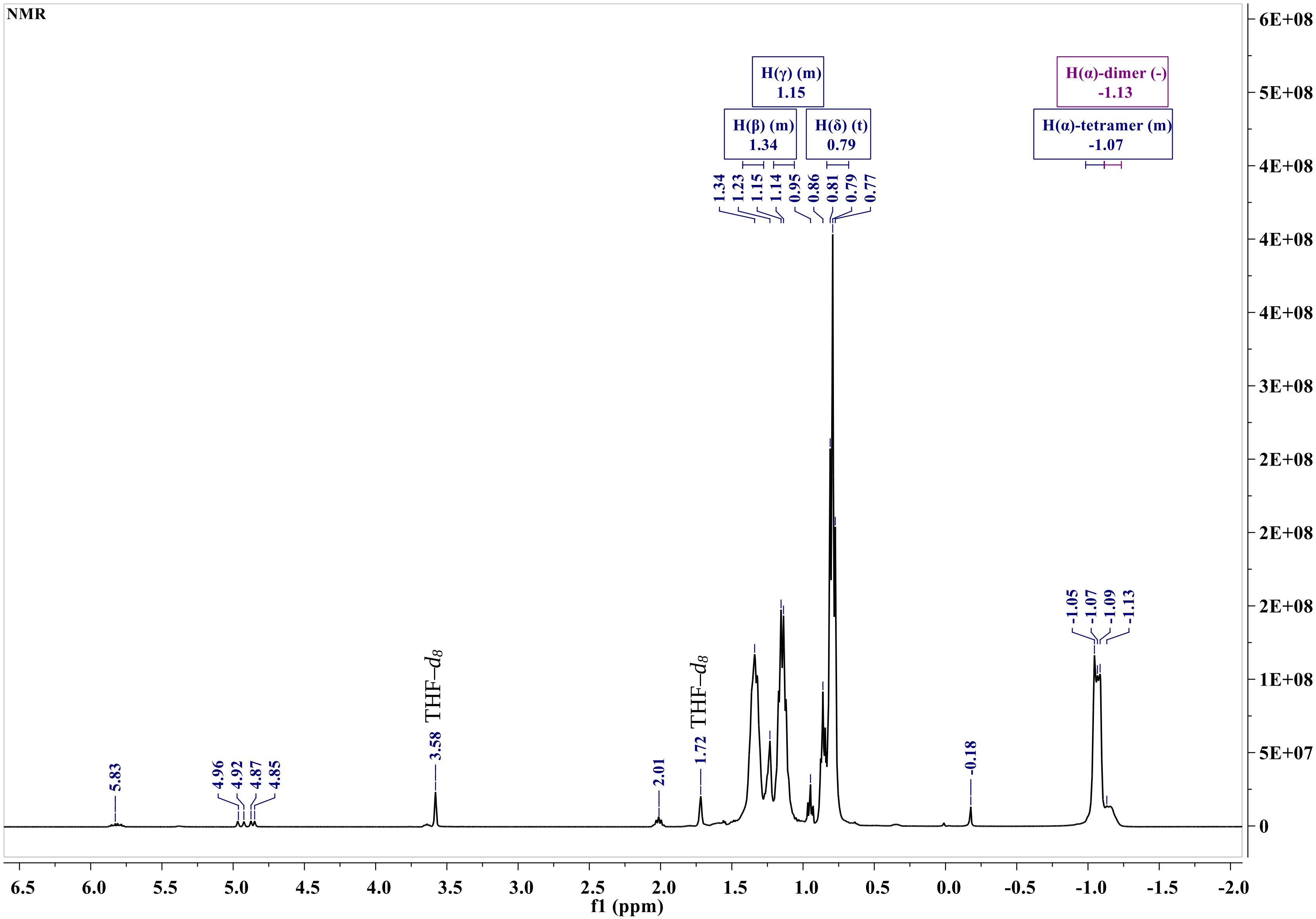


Figure B3. 1-Dimensional experimental ^{1}H NMR spectrum of *n*-BuLi in THF-d_8 at –213.15 Kelvin.

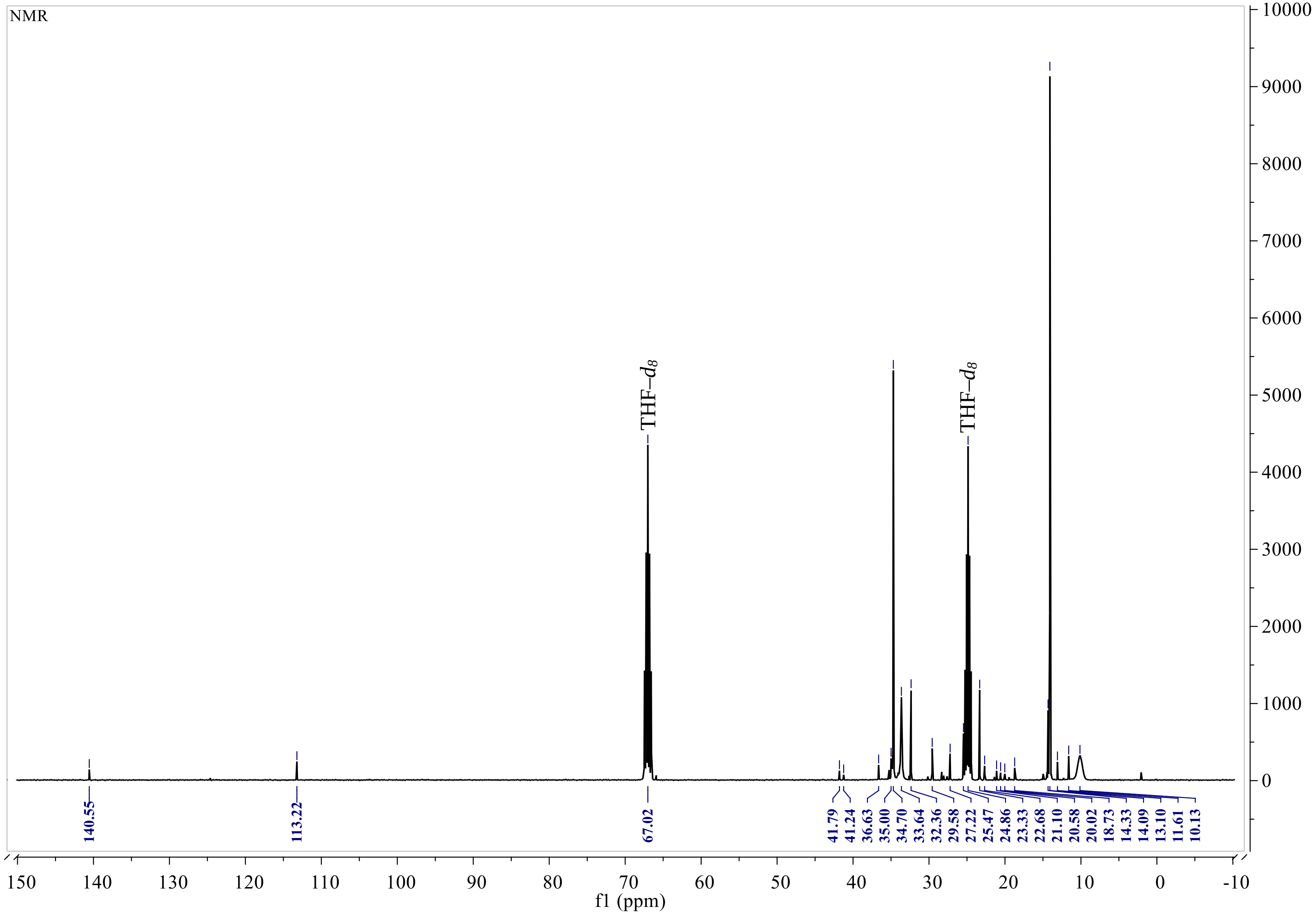


Figure B4. 1-Dimensional experimental ^{13}C NMR spectrum of *n*-BuLi in THF-d_8 at –233.15 Kelvin.

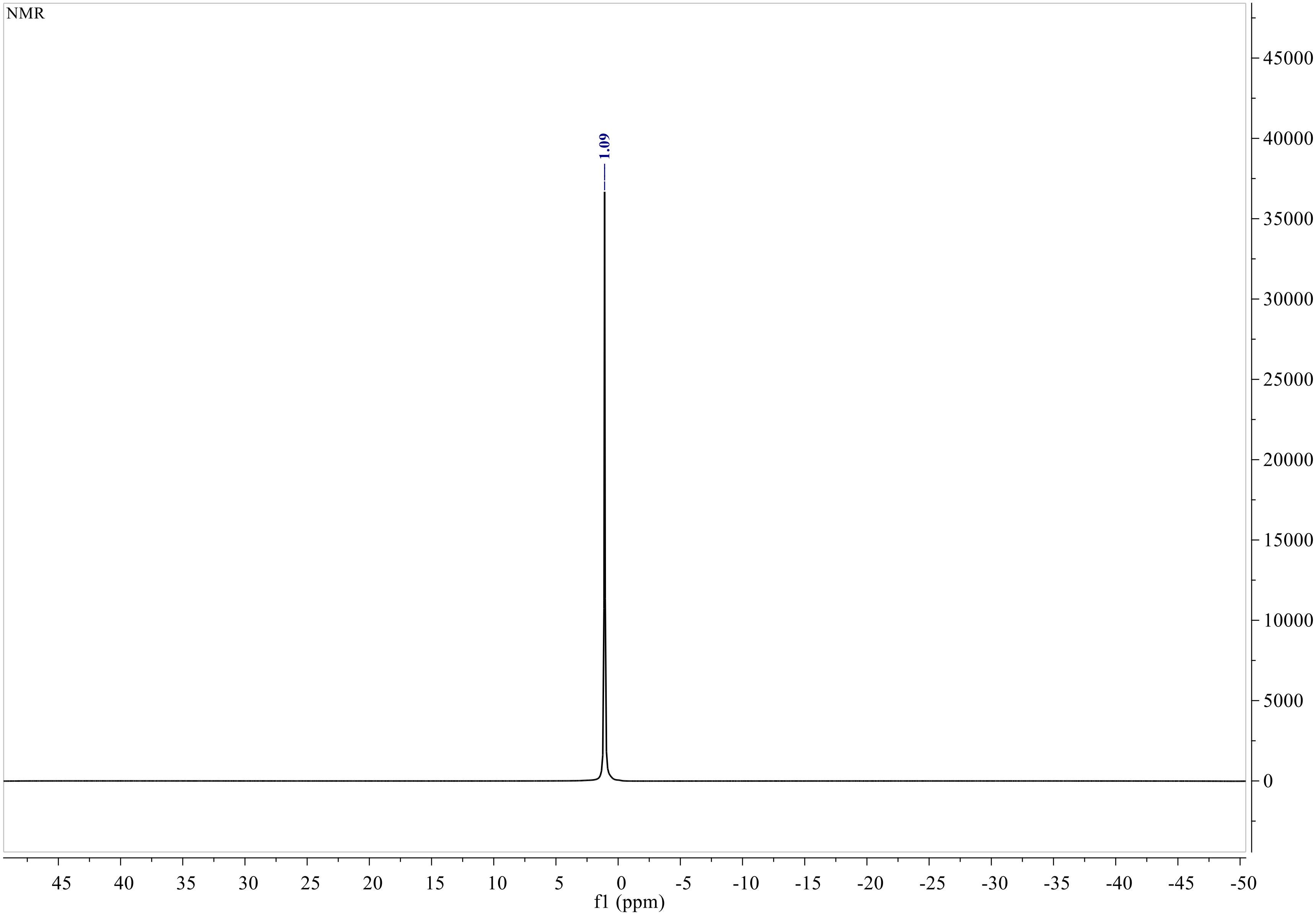


Figure B5. 1-Dimensional experimental ^{7}Li NMR spectrum of *n*-BuLi in THF-d_8 at –273.15 Kelvin.

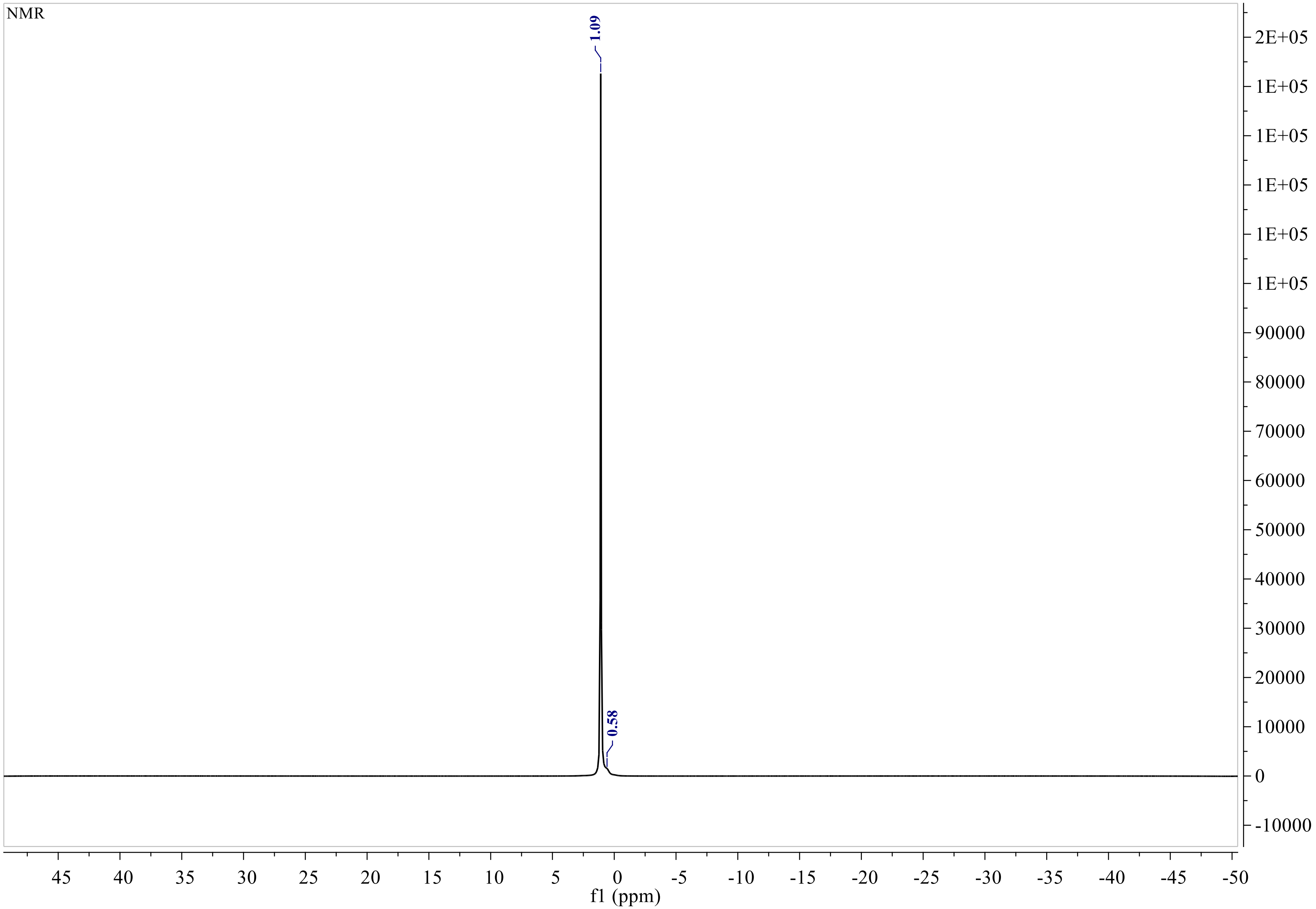


Figure B6. 1-Dimensional experimental ^{7}Li NMR spectrum of *n*-BuLi in THF-d_8 at –263.15 Kelvin.

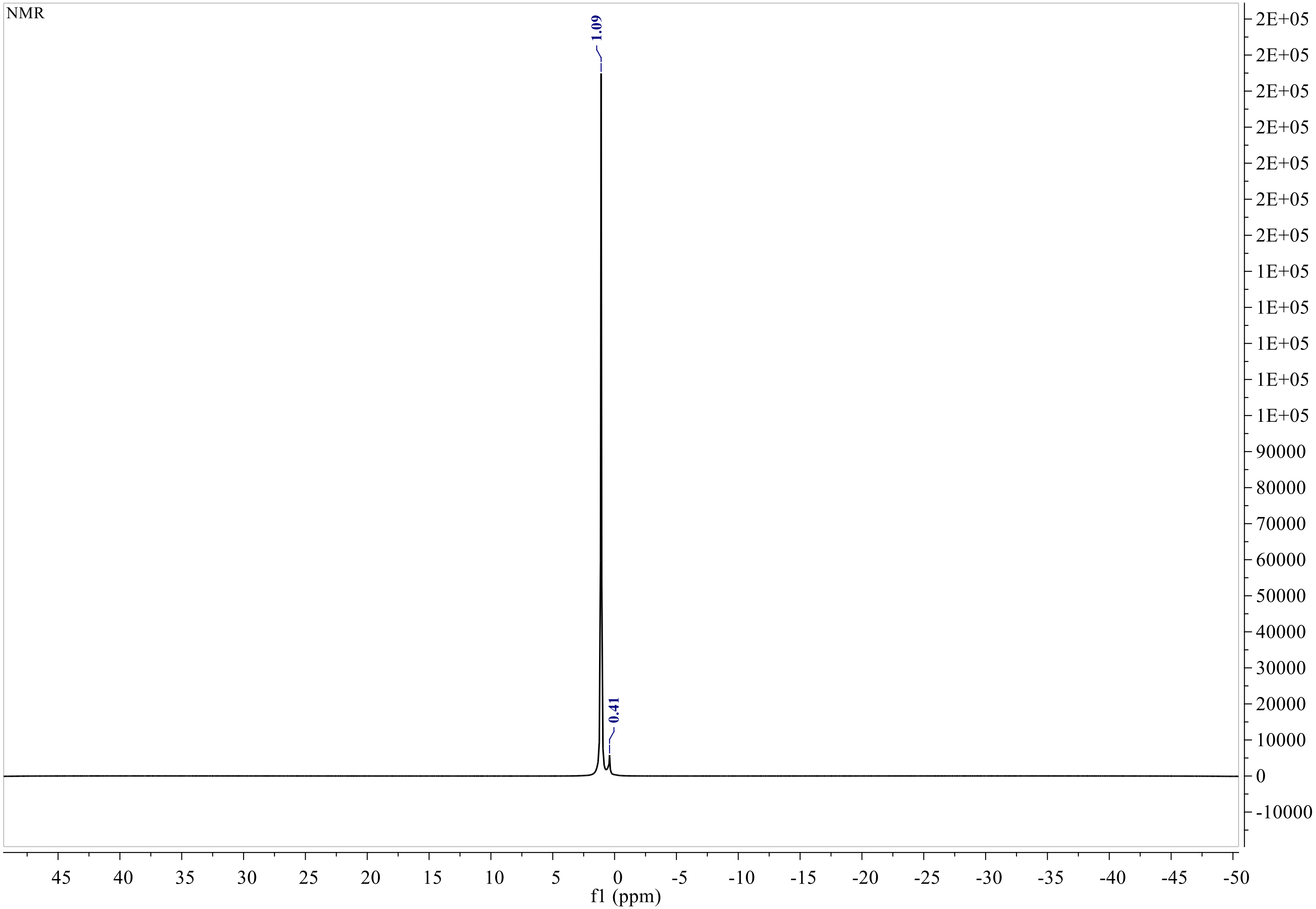


Figure B7. 1-Dimensional experimental ^{7}Li NMR spectrum of *n*-BuLi in THF-d_8 at –233.15 Kelvin.

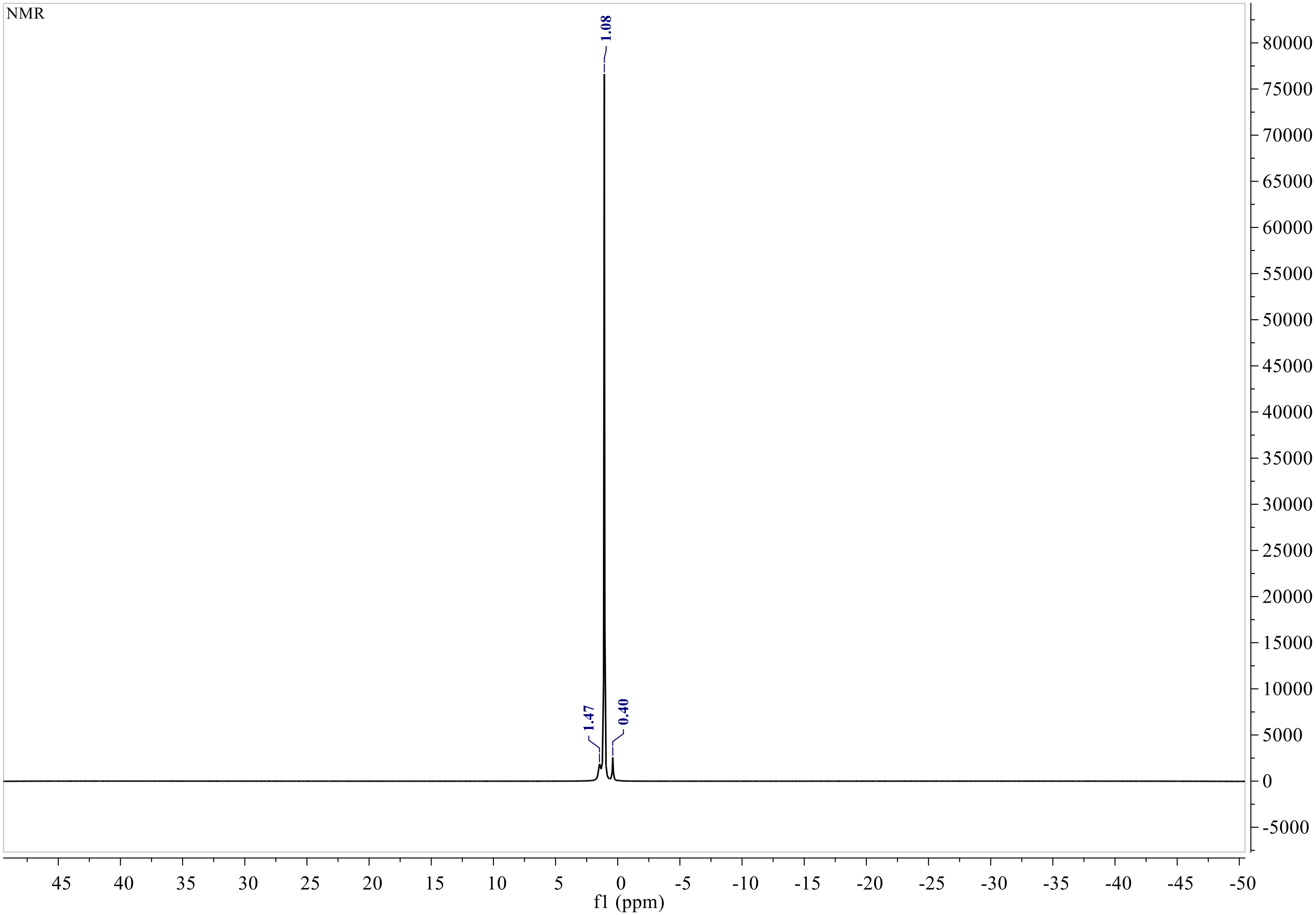


Figure B8. 1-Dimensional experimental ^{7}Li NMR spectrum of *n*-BuLi in THF-d_8 at –213.15 Kelvin.

Appendices

Appendix C:

Supporting Information for Chapter 5

Table C1. The computed geometric parameters for the β-halogenated structures; 3-chloro- and 3-bromothiophene.

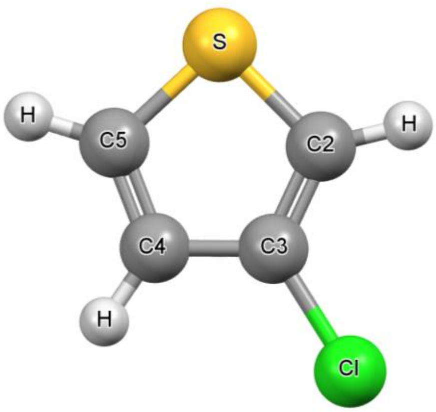
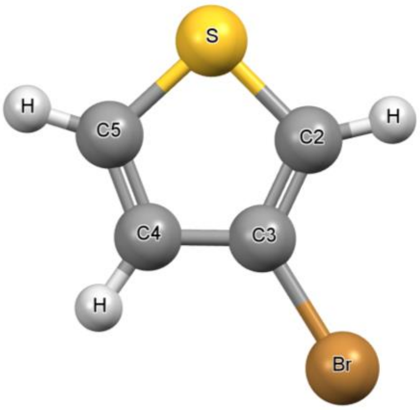
	Structures	
	C_4H_3SCl	**C_4H_3SBr**
		
	Theoretical	**Theoretical**
Bond Lengths (Å)		
C(2)–S	1.7239	1.7337
C(5)–S	1.7348	1.7347
C(2)–C(3)	1.3635	1.3633
C(3)–C(4)	1.4267	1.4273
C(4)–C(5)	1.3644	1.3647
C(2)–H	1.0783	1.0781
C(4)–H	1.0806	1.0805
C(5)–H	1.0794	1.0795
C(3)–X	1.7518	1.9086
Bond Angles (°)		
∠ CSC	91.81	91.79
∠ SC(5)C(4)	111.95	111.97
∠ SC(2)C(3)	110.33	110.35
∠ C(2)C(3)X	123.14	123.02
∠ C(4)C(3)X	122.41	122.54
∠ SC(2)H	121.25	121.02
∠ SC(5)H	119.97	119.96
∠ C(3)C(2)H	128.42	128.63
∠ C(3)C(4)H	123.92	124.06
∠ C(4)C(5)H	128.09	128.07
∠ C(5)C(4)H	124.62	124.48

Table C2. Cartesian coordinates and energies for 2-chlorothiophene found in Table 5.2. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-0.418708	0.202893	0.000000
2	6	C	0.292577	1.366802	0.000000
3	6	C	1.700780	1.126921	0.000100
4	6	C	2.021198	-0.199974	-0.000100
5	16	S	0.604411	-1.207793	0.000000
6	1	H	2.441369	1.915531	0.000100
7	1	H	2.999004	-0.657461	-0.000100
8	1	H	-0.168237	2.344396	0.000000
9	17	Cl	-2.148106	0.043669	0.000000

E(RB3LYP) = –1012.69661916 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.056999
Thermal correction to Energy = 0.059607
Thermal correction to Enthalpy 0.060225
Thermal correction to Gibbs Free Energy = 0.039116
Sum of electronic and zero-point Energies = -1012.639620
Sum of electronic and thermal Energies = -1012.637012
Sum of electronic and thermal Enthalpies = -1012.636394
Sum of electronic and thermal Free Energies = -1012.657503

Table C3. Cartesian coordinates and energies for 3-chlorothiophene found in Table C1. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-0.252985	-1.051995	-0.000002
2	6	C	0.579300	0.028017	-0.000002
3	6	C	-0.088918	1.288507	-0.000102
4	6	C	-1.444616	1.134788	0.000098
5	16	S	-1.907592	-0.537119	-0.000002
6	1	H	0.420868	2.241314	-0.000202
7	1	H	-2.201927	1.903977	0.000198
8	1	H	0.007230	-2.098392	0.000098
9	17	Cl	2.325802	-0.108758	-0.000002

E(RB3LYP) = –1012.70124706 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.056938
Thermal correction to Energy = 0.059526
Thermal correction to Enthalpy 0.060144
Thermal correction to Gibbs Free Energy = 0.039058
Sum of electronic and zero-point Energies = -1012.644309
Sum of electronic and thermal Energies = -1012.641721
Sum of electronic and thermal Enthalpies = -1012.641103
Sum of electronic and thermal Free Energies = -1012.662189

Table C4. Cartesian coordinates and energies for 2-bromothiophene found in Table 5.2. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-0.1458160	0.1960850	-0.0000080
2	6	C	-0.8522910	1.3644000	-0.0000080
3	6	C	-2.2618960	1.1329310	-0.0000080
4	6	C	-2.5896250	-0.1924620	0.0000920
5	16	S	-1.1784460	-1.2063930	-0.0000080
6	1	H	-0.3888700	2.3408900	-0.0000080
7	1	H	-2.9977790	1.9260460	-0.0001080
8	1	H	-3.5702340	-0.6439410	0.0000920
9	35	Br	1.7402800	0.0192450	-0.0000080

E(RB3LYP) = –3126.61807235 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.056436
Thermal correction to Energy = 0.059190
Thermal correction to Enthalpy 0.059808
Thermal correction to Gibbs Free Energy = 0.037871
Sum of electronic and zero-point Energies = -3126.561636
Sum of electronic and thermal Energies = -3126.558883
Sum of electronic and thermal Enthalpies = -3126.558265
Sum of electronic and thermal Free Energies = -3126.580202

Table C5. Cartesian coordinates and energies for 3-bromothiophene found in Table C1. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-0.835975	-1.038608	0.000090
2	6	C	-0.028380	0.059696	-0.000010
3	6	C	-0.725486	1.305193	-0.000110
4	6	C	-2.077585	1.120386	0.000090
5	16	S	-2.502677	-0.561416	-0.000010
6	1	H	-0.239990	2.270495	-0.000110
7	1	H	-2.852188	1.872283	0.000190
8	1	H	-0.556170	-2.079807	0.000090
9	35	Br	1.877021	-0.050295	-0.000010

E(RB3LYP) = –3126.62246140 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.056374
Thermal correction to Energy = 0.059107
Thermal correction to Enthalpy 0.059725
Thermal correction to Gibbs Free Energy = 0.037816
Sum of electronic and zero-point Energies = -3126.566088
Sum of electronic and thermal Energies = -3126.563355
Sum of electronic and thermal Enthalpies = -3126.562737
Sum of electronic and thermal Free Energies = -3126.584646

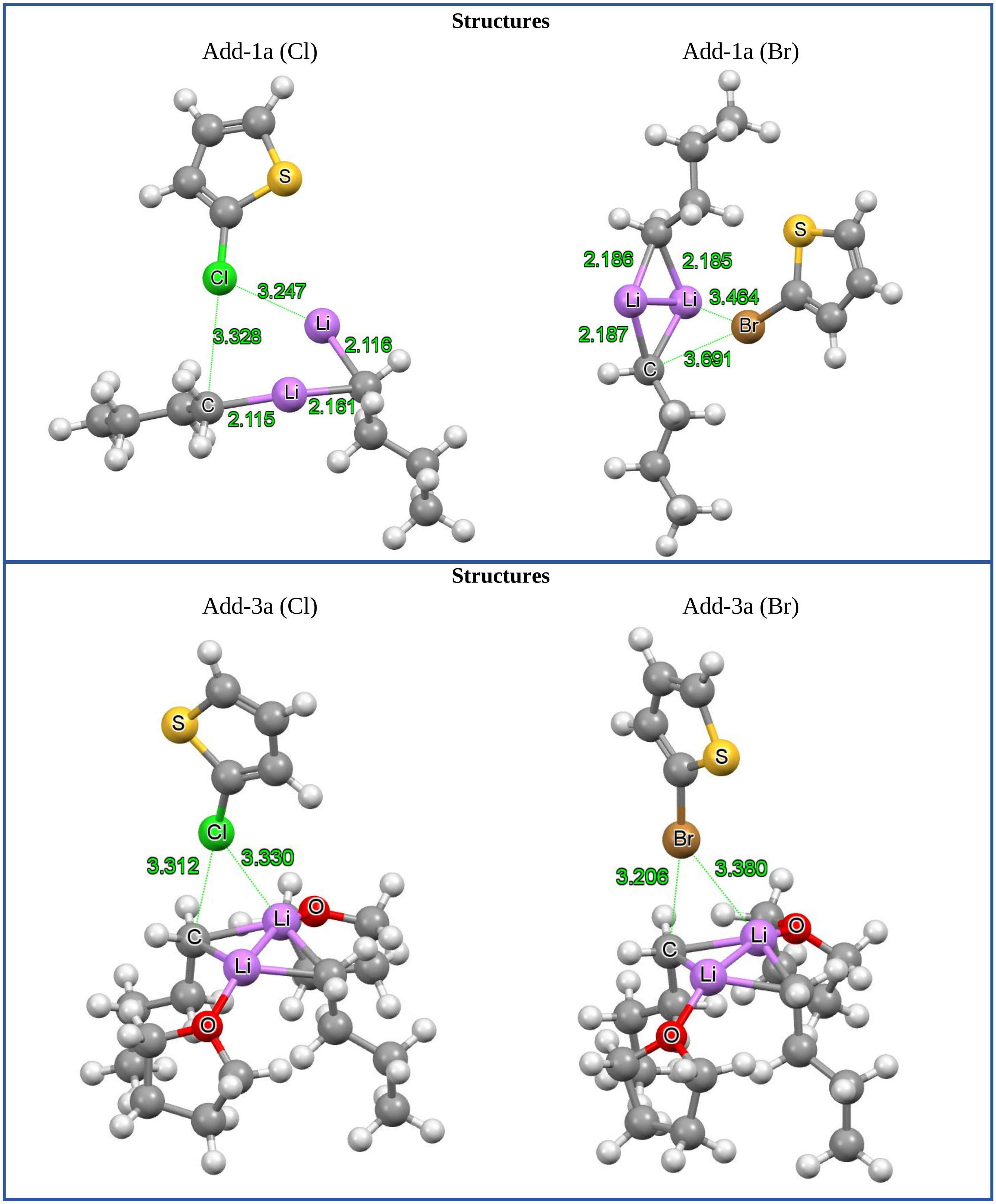
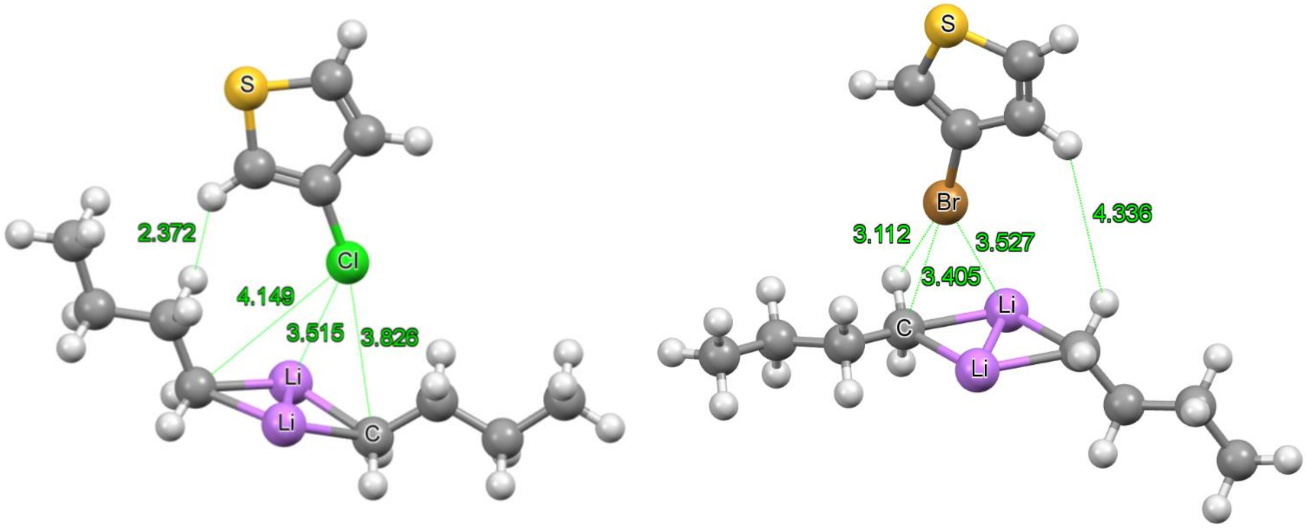


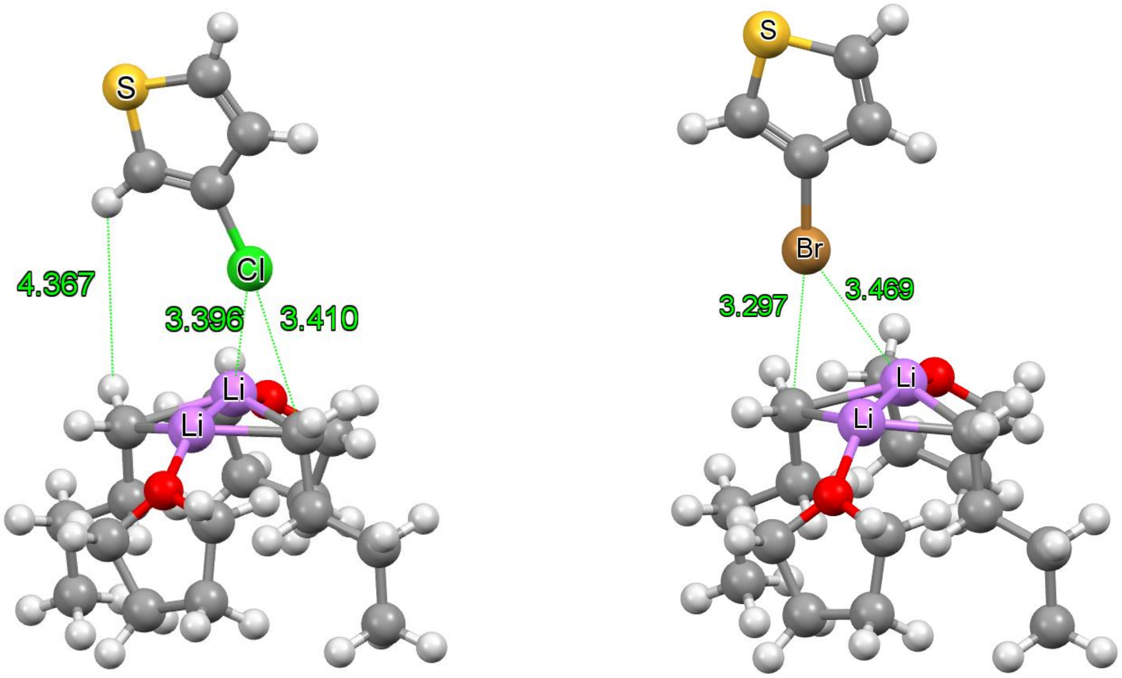
Figure C1. The computed adduct structures belonging to the 1st alpha step lithium-halogen exchange reactions.

Structures


Add-1b (Cl)

Add-1b (Br)

Structures

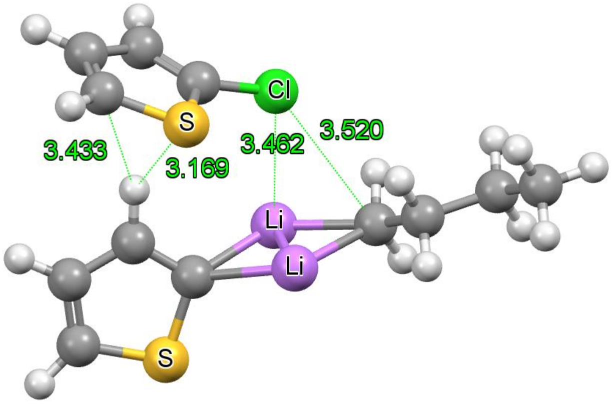

Add-3b (Cl)

Add-3b (Br)

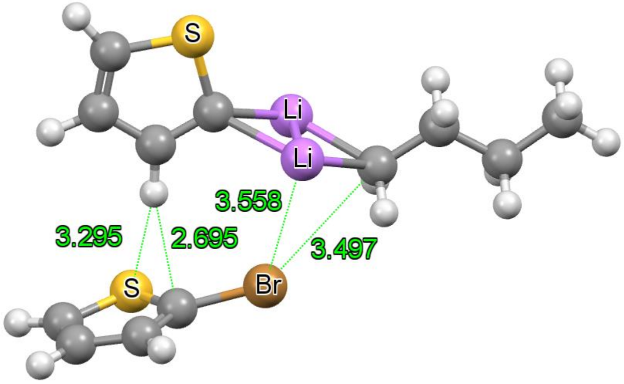
Figure C2. The computed adduct structures belonging to the 1st beta step lithium-halogen exchange reactions.

Structures

Add-2a (Cl)

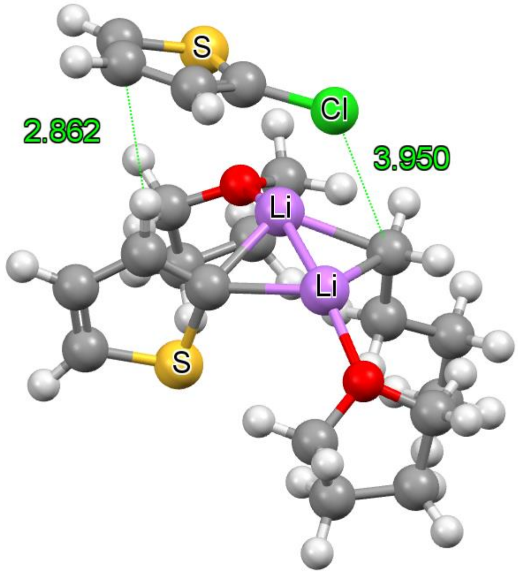


Add-2a (Br)

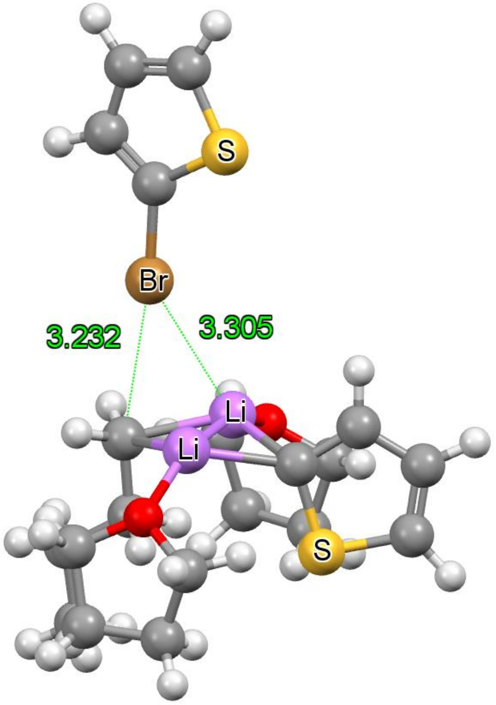


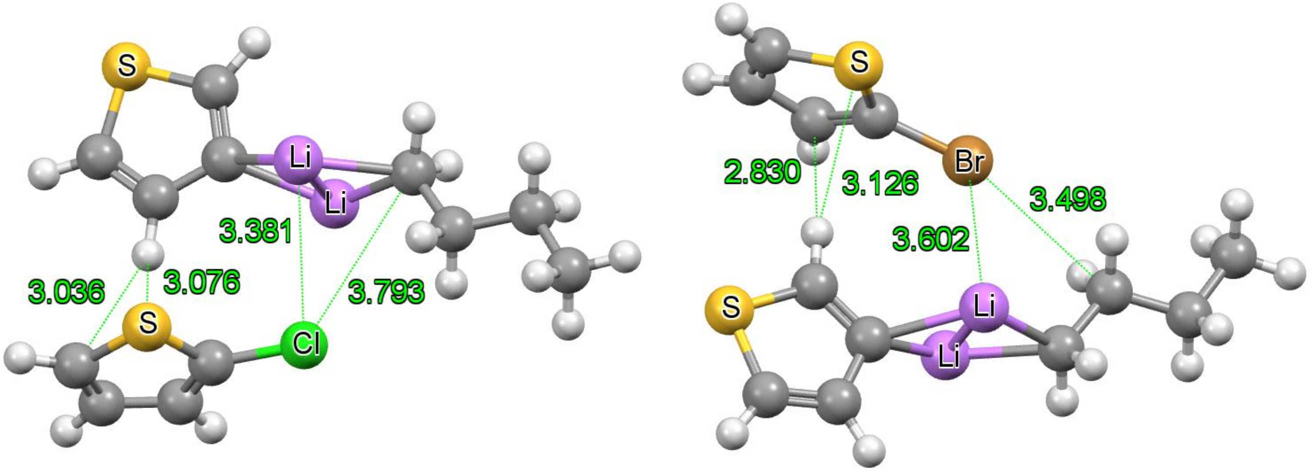
Structures

Add-4a (Cl)

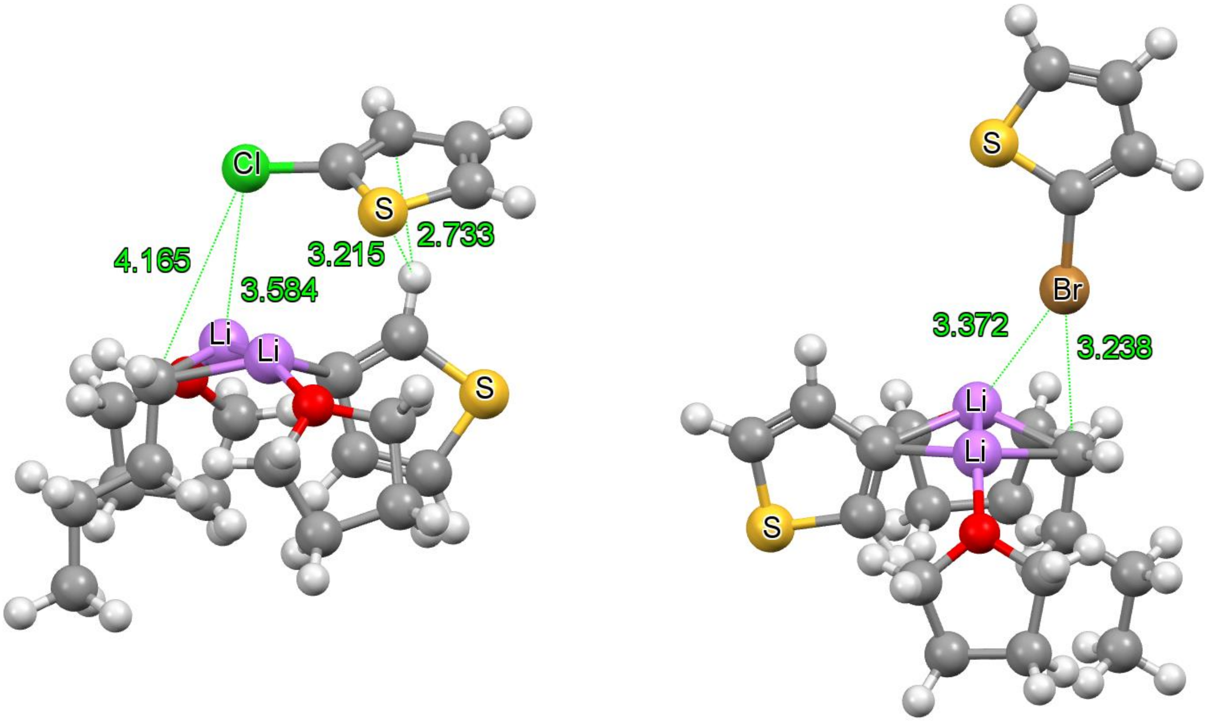


Add-4a (Br)




Structures

Add-2d (Cl) Add-2d (Br)

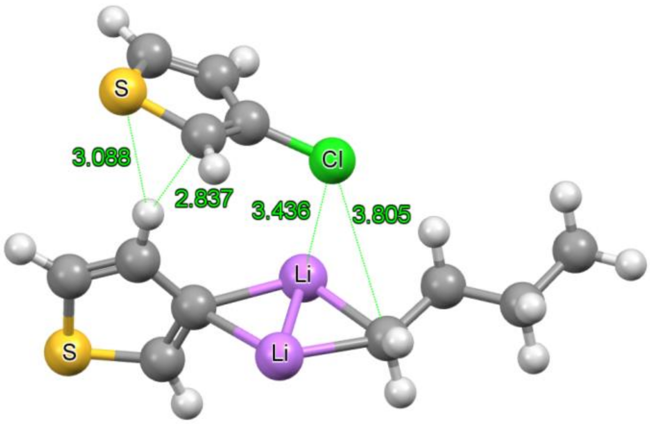

Structures

Add-4d (Cl) Add-4d (Br)

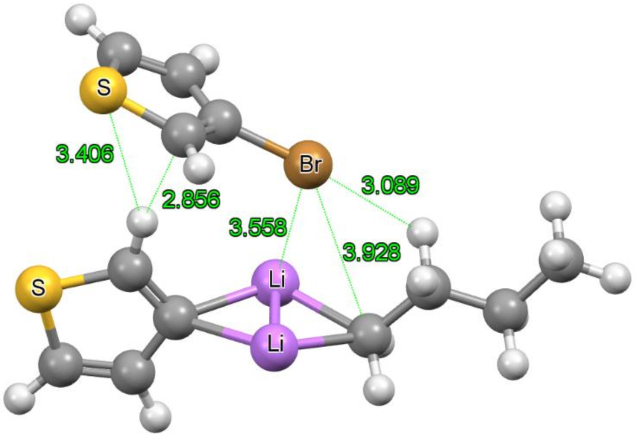
Figure C3. The computed adduct structures belonging to the 2nd alpha step lithium-halogen exchange reactions.

Structures

Add-2b (Cl)

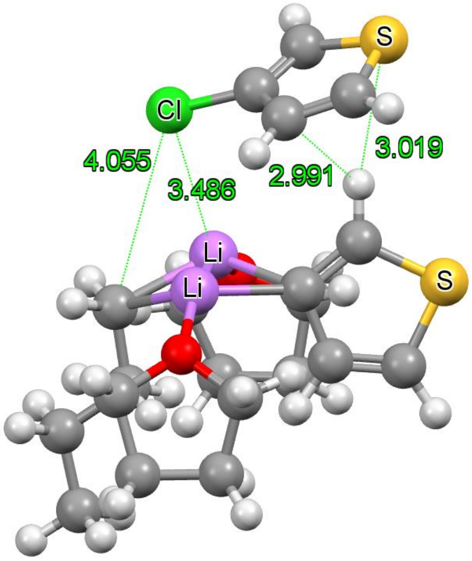


Add-2b (Br)

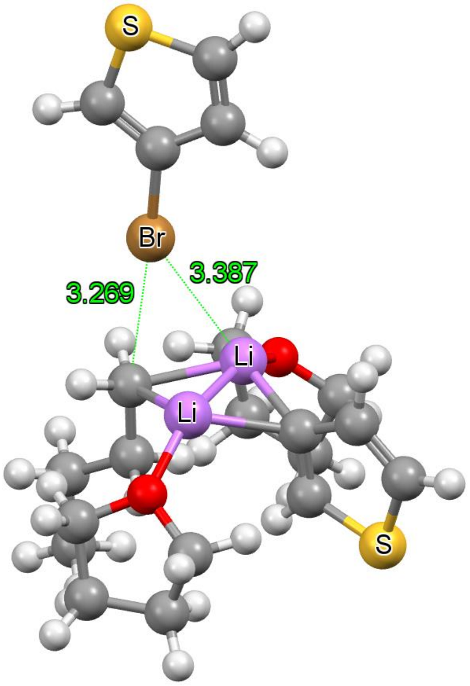


Structures

Add-4b (Cl)



Add-4b (Br)



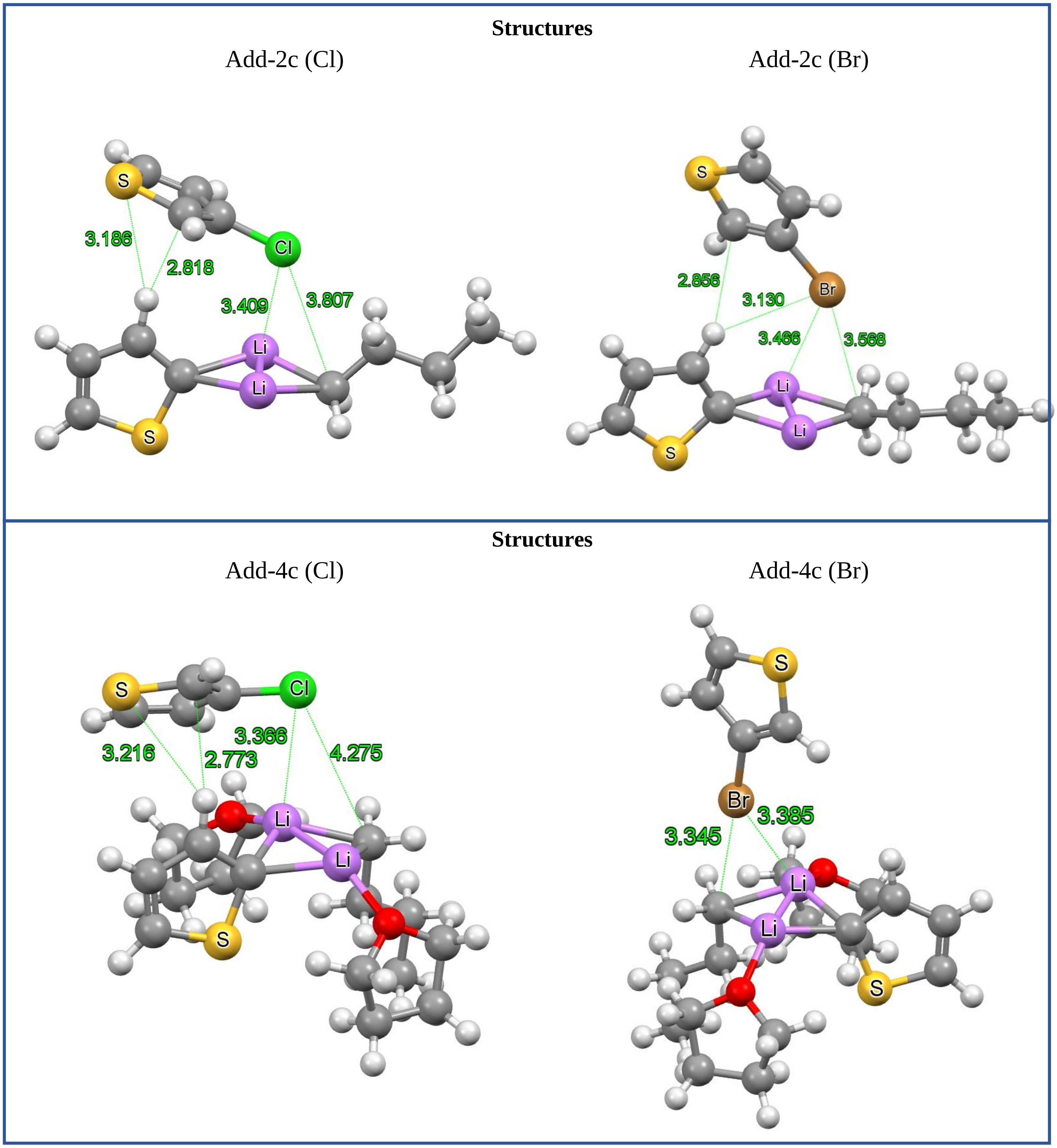


Figure C4. The computed adduct structures belonging to the 2nd beta step lithium-halogen exchange reactions.

Table C6. Cartesian coordinates and energies for Adduct **Add-1a (Cl)** found in Figure C1 and Figure 5.3. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	-0.95242	4.717924	-1.31424
2	1	H	-0.1767	4.228639	-1.91426
3	1	H	-0.74192	5.792516	-1.31297
4	1	H	-1.90808	4.567353	-1.82892
5	6	C	-0.99546	4.135597	0.104057
6	1	H	-0.03831	4.32232	0.608669
7	1	H	-1.75767	4.65883	0.696148
8	6	C	-1.28527	2.621312	0.150869
9	1	H	-0.52553	2.129566	-0.47844
10	1	H	-2.24101	2.452055	-0.37259
11	6	C	-1.32431	1.961956	1.541977
12	1	H	-2.10468	2.476254	2.137344
13	1	H	-0.38139	2.212951	2.063824
14	3	Li	-0.75376	-1.42814	-0.55894
15	6	C	-6.17119	-2.02545	-0.96684
16	1	H	-6.50396	-1.01634	-0.70066
17	1	H	-7.02079	-2.70218	-0.83201
18	1	H	-5.91846	-2.01693	-2.03284
19	6	C	-4.96421	-2.44552	-0.12007
20	1	H	-5.24723	-2.4724	0.940064
21	1	H	-4.66643	-3.46944	-0.38073
22	6	C	-3.74423	-1.52097	-0.2792
23	1	H	-4.06765	-0.49592	-0.03927
24	1	H	-3.48889	-1.48769	-1.35082
25	6	C	-2.49424	-1.88945	0.552128
26	1	H	-2.23015	-2.93861	0.312297
27	1	H	-2.81185	-1.96716	1.611578
28	3	Li	-1.80884	-0.09665	1.544683
29	6	C	2.942976	-0.32492	0.110378
30	6	C	3.935615	0.278095	-0.60446
31	6	C	4.929553	-0.65747	-1.02882
32	6	C	4.670012	-1.93757	-0.63342
33	16	S	3.195309	-2.04162	0.283801
34	1	H	3.955248	1.337996	-0.81568
35	1	H	5.801914	-0.38063	-1.60561
36	1	H	5.250297	-2.83013	-0.81178
37	17	Cl	1.535597	0.432828	0.796138

E(RB3LYP) = –1343.58257882 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.296797
Thermal correction to Energy = 0.308265
Thermal correction to Enthalpy 0.308883
Thermal correction to Gibbs Free Energy = 0.265242
Sum of electronic and zero-point Energies = -1343.285782
Sum of electronic and thermal Energies = -1343.274314
Sum of electronic and thermal Enthalpies = -1343.273696
Sum of electronic and thermal Free Energies = -1343.317337

Table C7. Cartesian coordinates and energies for Adduct **Add-1a (Br)** found in Figure C1 and Figure 5.3. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	-5.824007	-1.384749	-0.009413
2	1	H	-5.464114	-1.919050	-0.895572
3	1	H	-6.917385	-1.439229	-0.009490
4	1	H	-5.463704	-1.929621	0.870118
5	6	C	-5.320762	0.063541	-0.000900
6	1	H	-5.716771	0.598102	-0.874384
7	1	H	-5.716391	0.587731	0.878996
8	6	C	-3.786900	0.190516	-0.000530
9	1	H	-3.405429	-0.357941	-0.875436
10	1	H	-3.404911	-0.367993	0.867737
11	6	C	-3.222545	1.624221	0.007809
12	1	H	-3.682302	2.146483	0.874484
13	1	H	-3.685425	2.157992	-0.850283
14	3	Li	-1.496874	2.327588	-1.134461
15	6	C	3.985973	2.722040	-0.023550
16	1	H	4.060775	2.075722	0.857385
17	1	H	4.860402	3.380809	-0.030182
18	1	H	4.047231	2.075866	-0.905668
19	6	C	2.671882	3.512973	-0.013436
20	1	H	2.644141	4.172400	0.864066
21	1	H	2.632009	4.174321	-0.889040
22	6	C	1.411043	2.629233	-0.005719
23	1	H	1.481554	1.954095	0.861586
24	1	H	1.469682	1.956397	-0.875773
25	6	C	0.052783	3.363075	0.005026
26	1	H	0.046861	4.061174	-0.857453
27	1	H	0.057523	4.055562	0.871903
28	3	Li	-1.494429	2.326142	1.149019
29	6	C	1.215603	-1.749257	-0.000360
30	6	C	1.333385	-3.109607	-0.027702
31	6	C	2.699601	-3.527543	-0.022337
32	6	C	3.579462	-2.483815	0.008950
33	16	S	2.763271	-0.949038	0.032372
34	1	H	0.485807	-3.780181	-0.050584
35	1	H	3.006946	-4.564789	-0.041094
36	1	H	4.658684	-2.513766	0.019295
37	35	Br	-0.400192	-0.754412	0.003450

E(RB3LYP) = –3457.51734151 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.296201	
Thermal correction to Energy =	0.307796	
Thermal correction to Enthalpy	0.308414	
Thermal correction to Gibbs Free Energy =	0.263382	
Sum of electronic and zero-point Energies =	-3457.221141	
Sum of electronic and thermal Energies =	-3457.209545	
Sum of electronic and thermal Enthalpies =	-3457.208927	
Sum of electronic and thermal Free Energies =	-3457.253960	

Table C8. Cartesian coordinates and energies for Adduct **Add-3a (Cl)** found in Figure C1 and Figure 5.5. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-3.562375	1.473225	-3.286648
2	1	H	-4.132995	0.552364	-3.123350
3	1	H	-3.823974	1.856177	-4.278261
4	1	H	-3.905632	2.204553	-2.546421
5	6	C	-2.057346	1.216297	-3.144778
6	1	H	-1.729542	0.495863	-3.905330
7	1	H	-1.502107	2.141986	-3.346126
8	6	C	-1.651939	0.690565	-1.756629
9	1	H	-2.247849	-0.212423	-1.554917
10	1	H	-2.016467	1.415455	-1.013039
11	6	C	-0.155168	0.396884	-1.524454
12	1	H	0.422322	1.296563	-1.805932
13	1	H	0.167577	-0.354618	-2.268907
14	3	Li	-0.038251	0.999165	0.568232
15	6	C	-4.654379	-1.031681	2.702939
16	1	H	-5.012999	-0.033205	2.429590
17	1	H	-5.222659	-1.361750	3.578482
18	1	H	-4.900696	-1.704417	1.873882
19	6	C	-3.143811	-1.017320	2.966075
20	1	H	-2.919931	-0.354964	3.812337
21	1	H	-2.810948	-2.018713	3.269868
22	6	C	-2.310899	-0.568925	1.752235
23	1	H	-2.680845	0.419875	1.441227
24	1	H	-2.577410	-1.225856	0.910564
25	6	C	-0.778404	-0.524550	1.928231
26	1	H	-0.451651	-1.503817	2.327996
27	1	H	-0.551966	0.172220	2.757720
28	3	Li	-0.128673	-1.189643	-0.044369
29	6	C	-1.608985	-3.072297	-1.824087
30	8	O	-0.929106	-2.886408	-0.566177
31	6	C	-1.536816	-3.802776	0.374719
32	6	C	-3.001189	-3.986948	-0.085536
33	6	C	-3.076189	-3.223229	-1.430074
34	1	H	-1.393024	-2.207089	-2.449672
35	1	H	-1.224897	-3.976866	-2.312449
36	1	H	-0.984526	-4.747764	0.348115
37	1	H	-1.440628	-3.359984	1.364990
38	1	H	-3.230116	-5.045918	-0.216558
39	1	H	-3.702658	-3.580502	0.643727
40	1	H	-3.657175	-3.752056	-2.187118
41	1	H	-3.518966	-2.235447	-1.285759
42	6	C	-1.591427	3.167736	1.871845
43	8	O	-0.595577	2.835769	0.882858
44	6	C	-0.728119	3.805758	-0.183936
45	6	C	-2.212752	4.237038	-0.194610
46	6	C	-2.820595	3.538831	1.046478
47	1	H	-1.722611	2.298501	2.515451
48	1	H	-1.235506	4.013664	2.473450
49	1	H	-0.063965	4.649898	0.027480

50	1	H	-0.406653	3.319578	-1.104011
51	1	H	-2.295782	5.322635	-0.120307
52	1	H	-2.711937	3.924827	-1.112393
53	1	H	-3.512891	4.177833	1.596662
54	1	H	-3.351027	2.630420	0.753633
55	6	C	4.581976	-0.183825	0.132347
56	6	C	4.958049	-0.541127	1.394333
57	6	C	6.379260	-0.598454	1.531192
58	6	C	7.044060	-0.286399	0.380485
59	16	S	5.947575	0.090452	-0.916001
60	1	H	4.252226	-0.752254	2.185474
61	1	H	6.880361	-0.862460	2.452973
62	1	H	8.108657	-0.251788	0.204807
63	17	Cl	2.953424	0.002704	-0.452216

E(RB3LYP) = –1808.69451774 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.535147	
Thermal correction to Energy =	0.552651	
Thermal correction to Enthalpy	0.553269	
Thermal correction to Gibbs Free Energy =	0.495034	
Sum of electronic and zero-point Energies =	-1808.159371	
Sum of electronic and thermal Energies =	-1808.141866	
Sum of electronic and thermal Enthalpies =	-1808.141248	
Sum of electronic and thermal Free Energies =	-1808.199484	

Table C9. Cartesian coordinates and energies for Adduct **Add-3a (Br)** found in Figure C1 and Figure 5.5. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	5.051651	-0.897132	2.694480
2	1	H	5.300444	-1.578629	1.873365
3	1	H	5.638064	-1.201273	3.567437
4	1	H	5.386317	0.103688	2.399983
5	6	C	3.544728	-0.908235	2.977893
6	1	H	3.234861	-1.912415	3.296407
7	1	H	3.319696	-0.241406	3.820306
8	6	C	2.687533	-0.487835	1.771104
9	1	H	2.952141	-1.148829	0.932230
10	1	H	3.034947	0.503906	1.444683
11	6	C	1.157345	-0.468694	1.971543
12	1	H	0.933972	0.231974	2.798844
13	1	H	0.858338	-1.448994	2.390936
14	3	Li	0.304674	1.014014	0.637786
15	6	C	3.751069	1.276557	-3.209242
16	1	H	4.093282	2.042388	-2.504390
17	1	H	4.036622	1.599043	-4.215538
18	1	H	4.302404	0.357079	-2.984197
19	6	C	2.239559	1.052649	-3.082440
20	1	H	1.703462	1.974410	-3.343127
21	1	H	1.912909	0.296658	-3.807967
22	6	C	1.803212	0.610388	-1.674849

23	1	H	2.166831	1.369799	-0.966854
24	1	H	2.380286	-0.288777	-1.415050
25	6	C	0.294824	0.357595	-1.464608
26	1	H	-0.025378	-0.424852	-2.175223
27	1	H	-0.253586	1.252957	-1.803004
28	3	Li	0.393141	-1.204092	0.070467
29	6	C	1.923770	-3.753419	0.435479
30	8	O	1.228845	-2.874568	-0.478941
31	6	C	1.801020	-3.106260	-1.781745
32	6	C	3.300190	-3.228849	-1.513328
33	6	C	3.360819	-3.891891	-0.113380
34	1	H	1.870984	-3.300634	1.424380
35	1	H	1.406046	-4.718316	0.453176
36	1	H	1.385985	-4.033286	-2.196918
37	1	H	1.522371	-2.269769	-2.421626
38	1	H	3.809614	-3.812570	-2.281421
39	1	H	3.750555	-2.234687	-1.485559
40	1	H	3.646781	-4.942961	-0.178234
41	1	H	4.081788	-3.388153	0.531138
42	6	C	0.934375	3.804524	-0.225747
43	8	O	0.850591	2.865193	0.872122
44	6	C	1.875681	3.239728	1.815273
45	6	C	3.072460	3.598631	0.937468
46	6	C	2.416417	4.234714	-0.313172
47	1	H	0.571922	3.293699	-1.116834
48	1	H	0.279731	4.654583	-0.008189
49	1	H	1.529215	4.100107	2.401502
50	1	H	2.039526	2.392905	2.480863
51	1	H	3.767972	4.272002	1.440487
52	1	H	3.612251	2.689215	0.666007
53	1	H	2.500047	5.322621	-0.297951
54	1	H	2.881814	3.876409	-1.231957
55	6	C	-4.606676	-0.066794	-0.100117
56	6	C	-5.624518	0.435101	-0.860019
57	6	C	-6.906260	0.180340	-0.280592
58	6	C	-6.836736	-0.503968	0.898890
59	16	S	-5.191937	-0.858972	1.337565
60	1	H	-5.466577	0.962842	-1.790320
61	1	H	-7.838678	0.497079	-0.729164
62	1	H	-7.643452	-0.824220	1.541023
63	35	Br	-2.736692	0.042923	-0.470795

E(RB3LYP) = –3922.61817928 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.534882

Thermal correction to Energy = 0.552579

Thermal correction to Enthalpy 0.553197

Thermal correction to Gibbs Free Energy = 0.494205

Sum of electronic and zero-point Energies = -3922.083297

Sum of electronic and thermal Energies = -3922.065601

Sum of electronic and thermal Enthalpies = -3922.064983

Sum of electronic and thermal Free Energies = -3922.123974

Table C10. Cartesian coordinates and energies for Adduct **Add-1b (Cl)** found in Figure C2 and Figure 5.7. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	5.575822	-1.849550	-0.010441
2	1	H	5.136921	-2.332227	0.869757
3	1	H	6.647440	-2.073597	-0.012581
4	1	H	5.135664	-2.321452	-0.895847
5	6	C	5.303395	-0.340468	-0.001040
6	1	H	5.777412	0.115121	0.878304
7	1	H	5.776345	0.125858	-0.875331
8	6	C	3.806943	0.021452	0.002027
9	1	H	3.346070	-0.474944	0.870180
10	1	H	3.345125	-0.465354	-0.871116
11	6	C	3.459618	1.524099	0.010963
12	1	H	3.987467	1.988082	-0.849162
13	1	H	3.985861	1.977475	0.877602
14	3	Li	1.729238	2.244572	1.135963
15	6	C	-3.753075	2.821335	-0.002676
16	1	H	-3.842266	2.180797	-0.887405
17	1	H	-4.609011	3.503469	-0.001941
18	1	H	-3.842600	2.178407	0.880279
19	6	C	-2.416006	3.573151	-0.001403
20	1	H	-2.361644	4.232326	-0.877484
21	1	H	-2.362097	4.230050	0.876418
22	6	C	-1.186124	2.647362	-0.002225
23	1	H	-1.272896	1.980297	-0.874710
24	1	H	-1.273960	1.977582	0.868086
25	6	C	0.199994	3.322809	-0.000596
26	1	H	0.230633	4.016381	0.865010
27	1	H	0.232402	4.017243	-0.865339
28	3	Li	1.739272	2.245984	-1.127832
29	6	C	-2.312378	-0.935461	-0.003955
30	6	C	-1.128269	-1.611780	0.000651
31	6	C	-1.261563	-3.032987	0.005805
32	6	C	-2.571979	-3.413328	0.004906
33	16	S	-3.641911	-2.046622	-0.002077
34	1	H	-0.424009	-3.715899	0.009829
35	1	H	-2.975247	-4.414517	0.007951
36	1	H	-2.474632	0.129431	-0.008037
37	17	Cl	0.435519	-0.820003	0.000723

E(RB3LYP) = –1343.59967283 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.296945
Thermal correction to Energy = 0.308307
Thermal correction to Enthalpy 0.308925
Thermal correction to Gibbs Free Energy = 0.264418
Sum of electronic and zero-point Energies = -1343.302728
Sum of electronic and thermal Energies = -1343.291365
Sum of electronic and thermal Enthalpies = -1343.290747
Sum of electronic and thermal Free Energies = -1343.335255

Table C11. Cartesian coordinates and energies for Adduct **Add-1b (Br)** found in Figure C2 and Figure 5.7. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	0.067596	5.606051	0.851084
2	1	H	-0.616844	5.753973	1.693736
3	1	H	0.320783	6.593334	0.451857
4	1	H	0.986816	5.162381	1.249117
5	6	C	-0.562095	4.700684	-0.213877
6	1	H	-1.466275	5.175414	-0.616209
7	1	H	0.126554	4.590449	-1.061435
8	6	C	-0.928293	3.296630	0.302330
9	1	H	-1.592411	3.432437	1.173152
10	1	H	-0.011847	2.845748	0.711520
11	6	C	-1.576002	2.337925	-0.716674
12	1	H	-0.880908	2.267167	-1.577525
13	1	H	-2.460056	2.860938	-1.139475
14	3	Li	-2.327506	0.441872	-1.432063
15	6	C	-6.537305	-2.954657	0.220215
16	1	H	-7.065647	-2.302205	0.924150
17	1	H	-6.811141	-3.988137	0.455608
18	1	H	-6.917257	-2.730235	-0.782671
19	6	C	-5.022368	-2.729492	0.294589
20	1	H	-4.658833	-2.985547	1.298381
21	1	H	-4.512755	-3.414591	-0.395578
22	6	C	-4.588037	-1.288714	-0.033323
23	1	H	-5.123535	-0.614518	0.654040
24	1	H	-4.985310	-1.042074	-1.031271
25	6	C	-3.073642	-0.998460	0.017885
26	1	H	-2.573267	-1.733651	-0.646430
27	1	H	-2.714277	-1.310656	1.021522
28	3	Li	-2.302369	0.886272	0.785841
29	6	C	3.811084	-0.492140	-0.097263
30	6	C	2.533116	-0.965353	-0.050855
31	6	C	2.437099	-2.369897	0.188962
32	6	C	3.668452	-2.943198	0.321742
33	16	S	4.945440	-1.780096	0.156007
34	1	H	1.502043	-2.907561	0.256594
35	1	H	3.904421	-3.980197	0.507064
36	1	H	4.148016	0.518890	-0.262273
37	35	Br	0.993905	0.145985	-0.284292

E(RB3LYP) = –3457.51867393 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.296558

Thermal correction to Energy = 0.308009

Thermal correction to Enthalpy 0.308627

Thermal correction to Gibbs Free Energy = 0.264106

Sum of electronic and zero-point Energies = -3457.222116

Sum of electronic and thermal Energies = -3457.210665

Sum of electronic and thermal Enthalpies = -3457.210047

Sum of electronic and thermal Free Energies = -3457.254568

Table C12. Cartesian coordinates and energies for Adduct **Add-3b (Cl)** found in Figure C2 and Figure 5.8. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	3.980878	1.731689	-2.984088
2	1	H	4.233103	2.398990	-2.152393
3	1	H	4.338514	2.200664	-3.906375
4	1	H	4.546439	0.804449	-2.840475
5	6	C	2.473608	1.452746	-3.023985
6	1	H	1.928197	2.388400	-3.205726
7	1	H	2.238833	0.797058	-3.872356
8	6	C	1.931543	0.809049	-1.735354
9	1	H	2.206794	1.470315	-0.899439
10	1	H	2.513986	-0.106200	-1.549030
11	6	C	0.423335	0.488583	-1.686278
12	1	H	0.192904	-0.208124	-2.513968
13	1	H	-0.132954	1.403591	-1.965767
14	3	Li	0.176785	-1.169055	-0.298864
15	6	C	4.183128	-1.322843	3.133127
16	1	H	4.556454	-1.920455	2.294067
17	1	H	4.590947	-1.752052	4.053949
18	1	H	4.596483	-0.314177	3.023375
19	6	C	2.650181	-1.286888	3.140931
20	1	H	2.255887	-2.301740	3.283806
21	1	H	2.296265	-0.702344	3.999977
22	6	C	2.040584	-0.697214	1.856307
23	1	H	2.433365	-1.280166	1.008900
24	1	H	2.474928	0.303535	1.711895
25	6	C	0.501495	-0.616887	1.781840
26	1	H	0.152877	0.019302	2.617015
27	1	H	0.095202	-1.614637	2.039765
28	3	Li	-0.002323	0.984565	0.386255
29	6	C	0.806887	3.821729	-0.099121
30	8	O	0.505341	2.793906	0.874514
31	6	C	1.338119	3.053070	2.023169
32	6	C	2.682736	3.449906	1.419150
33	6	C	2.276918	4.232282	0.146604
34	1	H	0.629617	3.394419	-1.085083
35	1	H	0.122266	4.661622	0.056781
36	1	H	0.899741	3.869779	2.610604
37	1	H	1.360599	2.146956	2.627474
38	1	H	3.289225	4.041659	2.106410
39	1	H	3.242500	2.550234	1.154473
40	1	H	2.351565	5.309853	0.302682
41	1	H	2.911318	3.972410	-0.701279
42	6	C	1.495467	-3.827305	0.181447
43	8	O	1.021165	-2.862108	-0.787321
44	6	C	1.873227	-2.980954	-1.944347
45	6	C	3.270016	-3.155137	-1.354990
46	6	C	3.009850	-3.995462	-0.081112
47	1	H	1.263244	-3.433653	1.169985
48	1	H	0.953464	-4.766879	0.032854
49	1	H	1.567960	-3.857327	-2.530146

50	1	H	1.742551	-2.082410	-2.546197
51	1	H	3.957387	-3.639532	-2.050169
52	1	H	3.679782	-2.177462	-1.092583
53	1	H	3.255111	-5.046647	-0.242188
54	1	H	3.603027	-3.638510	0.761282
55	6	C	-4.828497	-0.424097	0.898589
56	6	C	-4.532685	-0.064330	-0.383111
57	6	C	-5.674439	0.145085	-1.213353
58	6	C	-6.836744	-0.064884	-0.529998
59	16	S	-6.545299	-0.516033	1.120294
60	1	H	-5.617204	0.434091	-2.253119
61	1	H	-7.849039	0.018140	-0.895372
62	1	H	-4.147273	-0.636273	1.707240
63	17	Cl	-2.890491	0.127053	-0.965756

E(RB3LYP) = –1808.69860640 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.534755		
Thermal correction to Energy =		0.552368		
Thermal correction to Enthalpy		0.552986		
Thermal correction to Gibbs Free Energy =		0.494257		
Sum of electronic and zero-point Energies =		-1808.163852		
Sum of electronic and thermal Energies =		-1808.146239		
Sum of electronic and thermal Enthalpies =		-1808.145621		
Sum of electronic and thermal Free Energies =		-1808.204349		

Table C13. Cartesian coordinates and energies for Adduct **Add-3b (Br)** found in Figure C2 and Figure 5.8. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	3.751985	1.218313	-3.367362
2	1	H	4.122841	1.996771	-2.691302
3	1	H	3.992354	1.524279	-4.390531
4	1	H	4.315072	0.303765	-3.151330
5	6	C	2.248005	0.994263	-3.170148
6	1	H	1.699476	1.911127	-3.422588
7	1	H	1.891047	0.226072	-3.868109
8	6	C	1.873425	0.575179	-1.737802
9	1	H	2.269641	1.346070	-1.059325
10	1	H	2.459171	-0.321397	-1.487603
11	6	C	0.376871	0.326645	-1.452952
12	1	H	0.025059	-0.469759	-2.133298
13	1	H	-0.189697	1.214538	-1.783989
14	3	Li	0.430518	-1.204688	0.115362
15	6	C	5.144194	-0.929904	2.661205
16	1	H	5.372027	-1.618411	1.839869
17	1	H	5.739714	-1.237169	3.526877
18	1	H	5.487160	0.065059	2.356546
19	6	C	3.641652	-0.919766	2.967182
20	1	H	3.323782	-1.917224	3.298669
21	1	H	3.437773	-0.243196	3.807200

22	6	C	2.771605	-0.497722	1.770127
23	1	H	3.009044	-1.172072	0.933850
24	1	H	3.132118	0.484163	1.427679
25	6	C	1.245506	-0.447366	1.995556
26	1	H	1.048596	0.267307	2.817488
27	1	H	0.933425	-1.416955	2.429886
28	3	Li	0.457479	1.019273	0.615639
29	6	C	1.082959	3.794328	-0.289479
30	8	O	1.000973	2.872156	0.823254
31	6	C	2.039721	3.249030	1.750380
32	6	C	3.230427	3.580794	0.854340
33	6	C	2.567079	4.214201	-0.393477
34	1	H	0.711169	3.272212	-1.170173
35	1	H	0.434793	4.651422	-0.080534
36	1	H	1.709297	4.121955	2.327301
37	1	H	2.200807	2.410397	2.426977
38	1	H	3.943034	4.248244	1.341075
39	1	H	3.751850	2.659964	0.585076
40	1	H	2.657803	5.301645	-0.383965
41	1	H	3.021587	3.848748	-1.314898
42	6	C	1.935511	-3.768974	0.537582
43	8	O	1.255430	-2.899141	-0.396926
44	6	C	1.838206	-3.152279	-1.690915
45	6	C	3.332994	-3.281304	-1.405089
46	6	C	3.371664	-3.943596	-0.004872
47	1	H	1.889680	-3.292959	1.515815
48	1	H	1.402006	-4.724513	0.576874
49	1	H	1.421643	-4.082283	-2.098184
50	1	H	1.571364	-2.322557	-2.344375
51	1	H	3.850120	-3.867414	-2.166236
52	1	H	3.786368	-2.288645	-1.371429
53	1	H	3.630643	-5.001718	-0.069291
54	1	H	4.102771	-3.458943	0.642822
55	6	C	-5.588990	-0.136882	-0.809056
56	6	C	-4.577185	-0.101427	0.104279
57	6	C	-5.012636	-0.202215	1.460964
58	6	C	-6.369953	-0.313647	1.549542
59	16	S	-7.123541	-0.296822	-0.013595
60	1	H	-4.344398	-0.191544	2.310427
61	1	H	-6.974902	-0.405052	2.438977
62	1	H	-5.526894	-0.079914	-1.884221
63	35	Br	-2.727547	0.063807	-0.374234

E(RB3LYP) = –3922.62148089 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.534447	
Thermal correction to Energy =	0.552217	
Thermal correction to Enthalpy	0.552835	
Thermal correction to Gibbs Free Energy =	0.493701	
Sum of electronic and zero-point Energies =	-3922.087034	
Sum of electronic and thermal Energies =	-3922.069264	
Sum of electronic and thermal Enthalpies =	-3922.068646	
Sum of electronic and thermal Free Energies =	-3922.127780	

Table C14. Cartesian coordinates and energies for Adduct **Add-2a (Cl)** found in Figure C3 and Figure 5.10. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	0.739517	1.827331	1.568803
2	6	C	5.831976	-0.344412	-0.953674
3	1	H	5.391772	-1.324627	-1.167126
4	1	H	6.869226	-0.506007	-0.643806
5	1	H	5.849802	0.219054	-1.893132
6	6	C	5.022834	0.398838	0.115452
7	1	H	5.040920	-0.167058	1.055668
8	1	H	5.493949	1.365910	0.332478
9	6	C	3.554316	0.644384	-0.279222
10	1	H	3.109721	-0.337813	-0.506350
11	1	H	3.566571	1.185085	-1.241314
12	6	C	2.679001	1.400516	0.741779
13	1	H	3.191300	2.357265	0.963116
14	1	H	2.750732	0.836304	1.696338
15	3	Li	1.028553	1.405100	-0.701367
16	6	C	-0.917688	1.998533	0.116260
17	6	C	-2.051712	1.202794	0.207766
18	6	C	-3.315863	1.845467	-0.005710
19	6	C	-3.190485	3.181156	-0.272465
20	16	S	-1.506302	3.624213	-0.255342
21	1	H	-1.987741	0.141826	0.428033
22	1	H	-4.271747	1.334920	0.037407
23	1	H	-3.971180	3.901938	-0.471503
24	6	C	-0.681313	-2.219494	0.440957
25	6	C	-1.737926	-2.613134	1.208362
26	6	C	-2.844476	-3.035019	0.409235
27	6	C	-2.604331	-2.949537	-0.931807
28	16	S	-1.006693	-2.350412	-1.265330
29	1	H	-1.728187	-2.592564	2.288899
30	1	H	-3.779998	-3.386373	0.823321
31	1	H	-3.258783	-3.203852	-1.751639
32	17	Cl	0.833609	-1.586039	0.999792

E(RB3LYP) = –1738.20054558 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.234039	
Thermal correction to Energy =	0.244640	
Thermal correction to Enthalpy	0.245258	
Thermal correction to Gibbs Free Energy =	0.203123	
Sum of electronic and zero-point Energies =	-1737.966506	
Sum of electronic and thermal Energies =	-1737.955906	
Sum of electronic and thermal Enthalpies =	-1737.955288	
Sum of electronic and thermal Free Energies =	-1737.997422	

Table C15. Cartesian coordinates and energies for Adduct **Add-2a (Br)** found in Figure C3 and Figure 5.10. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	6.804908	-1.207142	-0.129622
2	1	H	7.057378	-0.647685	-1.037113
3	1	H	7.398394	-2.126978	-0.130690
4	1	H	7.126982	-0.604716	0.726893
5	6	C	5.300368	-1.494799	-0.063466
6	1	H	5.006514	-2.123414	-0.914257
7	1	H	5.074890	-2.080441	0.837434
8	6	C	4.422377	-0.230214	-0.059882
9	1	H	4.677689	0.355830	-0.957222
10	1	H	4.746464	0.398271	0.784986
11	6	C	2.897156	-0.452529	0.005716
12	1	H	2.695627	-1.090158	0.892603
13	1	H	2.626459	-1.130210	-0.831891
14	3	Li	1.612104	0.847701	-1.159600
15	3	Li	1.701458	0.922658	1.184242
16	6	C	0.333744	2.196993	0.029716
17	6	C	-1.047084	2.065333	0.092629
18	16	S	0.641957	3.935611	-0.058085
19	6	C	-1.817166	3.275370	0.072470
20	1	H	-1.526573	1.093621	0.157057
21	6	C	-1.037365	4.396110	-0.008237
22	1	H	-2.900389	3.306366	0.115556
23	1	H	-1.350061	5.430439	-0.040184
24	6	C	-2.163699	-1.524729	0.203876
25	6	C	-2.954788	-1.276641	1.288584
26	6	C	-4.308526	-1.018276	0.912572
27	6	C	-4.511799	-1.071725	-0.436514
28	16	S	-3.046874	-1.443593	-1.294807
29	1	H	-2.587332	-1.270182	2.304969
30	1	H	-5.094364	-0.800553	1.623478
31	1	H	-5.428093	-0.920411	-0.986926
32	35	Br	-0.299839	-1.854847	0.216588

E(RB3LYP) = –3852.12350093 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.233137
Thermal correction to Energy = 0.244032
Thermal correction to Enthalpy 0.244650
Thermal correction to Gibbs Free Energy = 0.201452
Sum of electronic and zero-point Energies = -3851.890364
Sum of electronic and thermal Energies = -3851.879469
Sum of electronic and thermal Enthalpies = -3851.878851
Sum of electronic and thermal Free Energies = -3851.922049

Table C16. Cartesian coordinates and energies for Adduct **Add-4a (Cl)** found in Figure C3 and Figure 5.12. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	0.651999	1.483807	-0.485868
2	6	C	4.746372	-1.784430	-1.426172
3	1	H	5.176195	-1.092627	-0.693247
4	1	H	5.552370	-2.105052	-2.093948
5	1	H	4.398204	-2.665921	-0.876349
6	6	C	3.590712	-1.125883	-2.188650
7	1	H	3.962431	-0.261392	-2.754235
8	1	H	3.191058	-1.825592	-2.934142
9	6	C	2.438867	-0.663820	-1.278896
10	1	H	2.863986	0.018709	-0.527124
11	1	H	2.113129	-1.534891	-0.689932
12	6	C	1.222176	-0.004591	-1.959467
13	1	H	0.823119	-0.712126	-2.711065
14	1	H	1.582179	0.839035	-2.576983
15	3	Li	-0.386738	-0.606712	-0.695611
16	6	C	-0.798841	-3.095938	0.828656
17	8	O	-0.588376	-2.510344	-0.474209
18	6	C	0.111998	-3.498682	-1.262197
19	6	C	0.991780	-4.290495	-0.269366
20	6	C	0.518055	-3.809798	1.126030
21	1	H	-1.041844	-2.289447	1.519189
22	1	H	-1.640520	-3.798175	0.771438
23	1	H	-0.626364	-4.145172	-1.748657
24	1	H	0.677350	-2.965406	-2.025495
25	1	H	0.843308	-5.363988	-0.398808
26	1	H	2.050996	-4.079010	-0.421820
27	1	H	0.393352	-4.628558	1.836454
28	1	H	1.223859	-3.091731	1.546249
29	6	C	3.325027	2.804252	-0.896247
30	8	O	2.103718	2.736351	-0.122458
31	6	C	2.464159	3.053885	1.238817
32	6	C	3.779236	2.309924	1.450838
33	6	C	4.468387	2.411091	0.067453
34	1	H	3.211059	2.128589	-1.742373
35	1	H	3.446047	3.827393	-1.267287
36	1	H	2.589246	4.140020	1.334269
37	1	H	1.650829	2.719450	1.881321
38	1	H	4.376462	2.741527	2.255534
39	1	H	3.566050	1.268782	1.701026
40	1	H	5.248868	3.173934	0.065226
41	1	H	4.925346	1.463804	-0.220898
42	6	C	-0.300128	0.506017	1.221651
43	6	C	-1.516377	0.529475	1.888651
44	6	C	-1.532494	0.041301	3.237746
45	6	C	-0.301025	-0.379096	3.660996
46	16	S	0.859329	-0.166405	2.379066
47	1	H	-2.420217	0.890620	1.409189
48	1	H	-2.419856	0.004835	3.860640
49	1	H	-0.025112	-0.783897	4.624772

50	6	C	-3.460809	1.323668	-1.224566
51	6	C	-4.176609	2.112753	-0.373302
52	6	C	-5.071718	1.344368	0.432547
53	6	C	-5.011857	0.004660	0.177460
54	16	S	-3.856652	-0.365121	-1.067555
55	1	H	-5.727959	1.778499	1.174816
56	1	H	-5.571507	-0.795248	0.637785
57	1	H	-4.062186	3.186014	-0.318869
58	17	Cl	-2.247805	1.840596	-2.352645

E(RB3LYP) = –2203.30516725 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.472118		
Thermal correction to Energy =		0.488731		
Thermal correction to Enthalpy		0.489349		
Thermal correction to Gibbs Free Energy =		0.433586		
Sum of electronic and zero-point Energies =		-2202.833049		
Sum of electronic and thermal Energies =		-2202.816437		
Sum of electronic and thermal Enthalpies =		-2202.815819		
Sum of electronic and thermal Free Energies =		-2202.871581		

Table C17. Cartesian coordinates and energies for Adduct **Add-4a (Br)** found in Figure C3 and Figure 5.12. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	-4.115835	0.712173	-3.100137
2	1	H	-4.460282	-0.291943	-2.829950
3	1	H	-4.516984	0.946464	-4.091113
4	1	H	-4.562491	1.412080	-2.385618
5	6	C	-2.585457	0.794619	-3.064998
6	1	H	-2.158610	0.099654	-3.799342
7	1	H	-2.259357	1.796881	-3.371320
8	6	C	-1.988031	0.480940	-1.682355
9	1	H	-2.365353	-0.507710	-1.379762
10	1	H	-2.448419	1.169777	-0.959230
11	6	C	-0.449305	0.529972	-1.563647
12	1	H	-0.102298	1.527767	-1.879099
13	1	H	-0.020919	-0.145053	-2.324302
14	3	Li	-0.386601	1.247298	0.511951
15	3	Li	-0.317740	-1.063009	-0.143000
16	6	C	-1.360565	-3.068618	-2.088995
17	8	O	-0.956670	-2.785186	-0.728395
18	6	C	-1.826390	-3.556431	0.131263
19	6	C	-3.199333	-3.412859	-0.518819
20	6	C	-2.874051	-3.377224	-2.032590
21	1	H	-1.111192	-2.195218	-2.690497
22	1	H	-0.786641	-3.927535	-2.451269
23	1	H	-1.484929	-4.599218	0.140820

24	1	H	-1.755926	-3.140509	1.135528
25	1	H	-3.873950	-4.226811	-0.248987
26	1	H	-3.648024	-2.471441	-0.196804
27	1	H	-3.086037	-4.335529	-2.509851
28	1	H	-3.456358	-2.612069	-2.547204
29	6	C	-2.181214	3.243605	1.755684
30	8	O	-1.256225	2.984149	0.678256
31	6	C	-1.674915	3.819362	-0.425619
32	6	C	-3.211344	3.940693	-0.310613
33	6	C	-3.540676	3.305120	1.063915
34	1	H	-2.081349	2.435390	2.478838
35	1	H	-1.920909	4.198024	2.230466
36	1	H	-1.185999	4.794585	-0.329954
37	1	H	-1.337892	3.340203	-1.343409
38	1	H	-3.516591	4.987544	-0.352245
39	1	H	-3.713637	3.413554	-1.122374
40	1	H	-4.270111	3.881887	1.634495
41	1	H	-3.927465	2.291801	0.938399
42	6	C	-1.009722	-0.362069	1.834028
43	6	C	-0.428474	-1.153693	2.814619
44	6	C	-1.314121	-1.828724	3.720139
45	6	C	-2.631178	-1.569751	3.456953
46	16	S	-2.753954	-0.496462	2.089914
47	1	H	0.650470	-1.263546	2.893880
48	1	H	-0.984481	-2.474853	4.526450
49	1	H	-3.503562	-1.936961	3.979242
50	6	C	4.530649	0.177450	-0.372884
51	6	C	5.514866	0.273299	-1.314754
52	6	C	6.819109	0.134524	-0.746461
53	6	C	6.798811	-0.062984	0.604420
54	16	S	5.174385	-0.084648	1.224726
55	1	H	5.318028	0.435711	-2.365349
56	1	H	7.731666	0.180856	-1.326106
57	1	H	7.631307	-0.197491	1.278608
58	35	Br	2.647447	0.298585	-0.669366

E(RB3LYP) = –4317.22494028 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.471178		
Thermal correction to Energy =		0.488291		
Thermal correction to Enthalpy		0.488909		
Thermal correction to Gibbs Free Energy =		0.430453		
Sum of electronic and zero-point Energies =		-4316.753762		
Sum of electronic and thermal Energies =		-4316.736649		
Sum of electronic and thermal Enthalpies =		-4316.736031		
Sum of electronic and thermal Free Energies =		-4316.794487		

Table C18. Cartesian coordinates and energies for Adduct **Add-2d (Cl)** found in Figure C3 and Figure 5.20. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	0.814536	-1.364887	-0.968856
2	6	C	6.137505	0.063828	-0.227163
3	1	H	5.929336	0.638700	-1.136336
4	1	H	7.176520	-0.276773	-0.280081
5	1	H	6.056111	0.752410	0.621165
6	6	C	5.156121	-1.105147	-0.081961
7	1	H	5.275993	-1.795035	-0.927548
8	1	H	5.400247	-1.684649	0.817934
9	6	C	3.680499	-0.673362	-0.005190
10	1	H	3.467826	-0.062502	-0.897303
11	1	H	3.582299	0.026921	0.839452
12	6	C	2.636336	-1.800588	0.126711
13	1	H	2.910969	-2.394530	1.024210
14	1	H	2.823105	-2.521616	-0.696456
15	3	Li	0.834394	-1.591900	1.322810
16	6	C	-1.401716	-3.075799	-0.095011
17	6	C	-1.013101	-1.783307	0.166632
18	6	C	-2.210485	-0.977701	0.323310
19	6	C	-3.403095	-1.636890	0.185815
20	16	S	-3.156206	-3.321992	-0.153364
21	1	H	-2.186782	0.085565	0.536531
22	1	H	-4.406753	-1.240505	0.260089
23	1	H	-0.788368	-3.953779	-0.264463
24	6	C	-0.410039	2.262846	0.250692
25	6	C	-1.224180	2.621623	1.284459
26	6	C	-2.529722	2.982306	0.829278
27	6	C	-2.673389	2.887619	-0.524854
28	16	S	-1.208449	2.355218	-1.294097
29	1	H	-0.909046	2.620201	2.318277
30	1	H	-3.326566	3.296082	1.490041
31	1	H	-3.544189	3.097301	-1.127115
32	17	Cl	1.232858	1.715199	0.360166
33					

E(RB3LYP) = –1738.19008172 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.233932	
Thermal correction to Energy =	0.244431	
Thermal correction to Enthalpy	0.245049	
Thermal correction to Gibbs Free Energy =	0.203711	
Sum of electronic and zero-point Energies =	-1737.956149	
Sum of electronic and thermal Energies =	-1737.945650	
Sum of electronic and thermal Enthalpies =	-1737.945032	
Sum of electronic and thermal Free Energies =	-1737.986371	

Table C19. Cartesian coordinates and energies for Adduct **Add-2d (Br)** found in Figure C3 and Figure 5.20. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-0.953330	1.891377	1.185785
2	6	C	-6.044295	-0.340406	0.039930
3	1	H	-5.835411	-0.898878	-0.879287
4	1	H	-7.121813	-0.151041	0.075988
5	1	H	-5.792598	-0.992632	0.883445
6	6	C	-5.230293	0.957982	0.089434
7	1	H	-5.517752	1.607667	-0.747413
8	1	H	-5.475725	1.514367	1.003390
9	6	C	-3.707484	0.737581	0.041220
10	1	H	-3.489395	0.156489	-0.869577
11	1	H	-3.445166	0.064437	0.873077
12	6	C	-2.819658	1.997627	0.084815
13	1	H	-3.110008	2.573666	0.988345
14	1	H	-3.157685	2.665261	-0.735733
15	3	Li	-1.018518	2.008501	-1.115577
16	6	C	1.868087	1.492812	-0.106392
17	6	C	0.830807	2.387081	0.002456
18	6	C	1.399314	3.720356	0.106047
19	6	C	2.767164	3.799922	0.075772
20	16	S	3.480152	2.225626	-0.085375
21	1	H	0.795239	4.618818	0.203516
22	1	H	3.395808	4.677805	0.138336
23	1	H	1.833362	0.416044	-0.203479
24	6	C	0.826093	-2.016377	-0.205407
25	6	C	1.621034	-2.183333	-1.302978
26	6	C	2.947197	-2.575285	-0.944786
27	6	C	3.127513	-2.693112	0.403532
28	16	S	1.673433	-2.329488	1.283172
29	1	H	1.280433	-2.022416	-2.316005
30	1	H	3.731649	-2.757202	-1.667125
31	1	H	4.020234	-2.972808	0.942264
32	35	Br	-0.976168	-1.435615	-0.193342

E(RB3LYP) = –3852.11242621 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.233638		
Thermal correction to Energy =		0.244210		
Thermal correction to Enthalpy		0.244829		
Thermal correction to Gibbs Free Energy =		0.202941		
Sum of electronic and zero-point Energies =		-3851.878788		
Sum of electronic and thermal Energies =		-3851.868216		
Sum of electronic and thermal Enthalpies =		-3851.867598		
Sum of electronic and thermal Free Energies =		-3851.909486		

Table C20. Cartesian coordinates and energies for Adduct **Add-4d (Cl)** found in Figure C3 and Figure 5.21. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-0.936727	-1.435076	-0.549163
2	6	C	-5.096605	1.825906	-1.301161
3	1	H	-5.444531	1.197734	-0.473574
4	1	H	-5.966949	2.076855	-1.915875
5	1	H	-4.716189	2.756727	-0.866069
6	6	C	-4.004692	1.114509	-2.108828
7	1	H	-4.413829	0.202686	-2.563588
8	1	H	-3.685640	1.751496	-2.943801
9	6	C	-2.767485	0.736702	-1.275447
10	1	H	-3.112072	0.112368	-0.437738
11	1	H	-2.402741	1.654545	-0.790006
12	6	C	-1.609397	0.038876	-2.017799
13	1	H	-1.269124	0.714323	-2.826007
14	1	H	-2.029261	-0.822435	-2.572615
15	3	Li	0.191048	0.549636	-0.948762
16	6	C	1.464741	2.845901	0.363099
17	8	O	0.708724	2.402739	-0.793307
18	6	C	-0.143740	3.495848	-1.185062
19	6	C	-0.639388	4.062598	0.141610
20	6	C	0.596652	3.917605	1.060241
21	1	H	1.652848	1.967802	0.977929
22	1	H	2.418084	3.257349	0.015798
23	1	H	0.444717	4.232720	-1.746746
24	1	H	-0.924864	3.093587	-1.829952
25	1	H	-0.987455	5.093006	0.053458
26	1	H	-1.464023	3.449361	0.511816
27	1	H	1.141124	4.860705	1.138665
28	1	H	0.315043	3.602338	2.064760
29	6	C	-3.684354	-2.658826	-0.499831
30	8	O	-2.388456	-2.540860	0.133800
31	6	C	-2.608113	-2.646270	1.556823
32	6	C	-3.880126	-1.837122	1.790509
33	6	C	-4.716101	-2.122478	0.519682
34	1	H	-3.645381	-2.085794	-1.425529
35	1	H	-3.863439	-3.712468	-0.737584
36	1	H	-2.742739	-3.702215	1.824142
37	1	H	-1.723951	-2.250082	2.054500
38	1	H	-4.393491	-2.124144	2.709504
39	1	H	-3.627029	-0.776827	1.855430
40	1	H	-5.486957	-2.870869	0.711926
41	1	H	-5.208963	-1.221563	0.152996
42	6	C	1.370127	-0.722282	1.642255
43	6	C	0.184533	-0.428600	1.022160
44	6	C	-0.602645	0.396834	1.923704
45	6	C	-0.027726	0.694503	3.130580
46	16	S	1.547649	-0.024577	3.265926
47	1	H	-1.586740	0.779601	1.667343
48	1	H	-0.424666	1.288955	3.942410
49	1	H	2.211299	-1.293008	1.272528

50	6	C	3.242397	-1.495920	-1.391207
51	6	C	3.949734	-2.322695	-0.568312
52	6	C	4.862324	-1.594028	0.254521
53	6	C	4.823337	-0.246392	0.039060
54	16	S	3.668253	0.179453	-1.186203
55	1	H	5.514415	-2.060602	0.980585
56	1	H	5.397189	0.530265	0.521156
57	1	H	3.817274	-3.395058	-0.544824
58	17	Cl	2.008686	-1.961889	-2.521551

E(RB3LYP) = –2203.29307662 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.471735
Thermal correction to Energy = 0.488465
Thermal correction to Enthalpy 0.489083
Thermal correction to Gibbs Free Energy = 0.432648
Sum of electronic and zero-point Energies = -2202.821341
Sum of electronic and thermal Energies = -2202.804612
Sum of electronic and thermal Enthalpies = -2202.803994
Sum of electronic and thermal Free Energies = -2202.860429

Table C21. Cartesian coordinates and energies for Adduct **Add-4d (Br)** found in Figure C3 and Figure 5.21. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	0.334319	1.107618	0.638790
2	6	C	3.839202	1.375879	-3.246366
3	1	H	4.291498	1.996999	-2.465388
4	1	H	4.150273	1.780081	-4.214730
5	1	H	4.266455	0.371517	-3.151732
6	6	C	2.313445	1.337400	-3.100778
7	1	H	1.901568	2.346702	-3.228867
8	1	H	1.878278	0.728085	-3.903132
9	6	C	1.844058	0.780498	-1.745677
10	1	H	2.312506	1.390579	-0.960020
11	1	H	2.301710	-0.212628	-1.622777
12	6	C	0.319018	0.699781	-1.517650
13	1	H	-0.119520	0.100955	-2.334909
14	1	H	-0.108980	1.703779	-1.679260
15	3	Li	0.310160	-1.073397	-0.273131
16	6	C	1.978434	-3.489972	-0.365401
17	8	O	1.028420	-2.676468	-1.089097
18	6	C	1.390838	-2.766061	-2.486409
19	6	C	2.924361	-2.958661	-2.520168
20	6	C	3.312603	-3.175460	-1.036092
21	1	H	1.926613	-3.204942	0.684465
22	1	H	1.703266	-4.546095	-0.478478
23	1	H	0.867864	-3.620176	-2.929096

24	1	H	1.050592	-1.851132	-2.970186
25	1	H	3.187444	-3.822074	-3.133604
26	1	H	3.426558	-2.086053	-2.939641
27	1	H	4.043406	-3.974131	-0.900764
28	1	H	3.721382	-2.259113	-0.606062
29	6	C	1.426853	3.864631	0.086763
30	8	O	1.198039	2.812701	1.052516
31	6	C	2.257177	2.910715	2.028636
32	6	C	3.500896	3.201572	1.192451
33	6	C	2.956803	4.079946	0.038549
34	1	H	0.999777	3.535411	-0.859667
35	1	H	0.904012	4.766669	0.421417
36	1	H	2.032104	3.730779	2.722146
37	1	H	2.291480	1.966606	2.570388
38	1	H	4.282631	3.696786	1.770331
39	1	H	3.905080	2.264405	0.803945
40	1	H	3.199578	5.133062	0.189925
41	1	H	3.371778	3.776490	-0.923244
42	6	C	2.523362	-0.633144	1.623182
43	6	C	1.152386	-0.629377	1.696560
44	6	C	0.764253	-1.396855	2.864445
45	6	C	1.786487	-1.935058	3.602387
46	16	S	3.331011	-1.533073	2.917604
47	1	H	-0.270890	-1.553855	3.155350
48	1	H	1.731129	-2.535231	4.500499
49	1	H	3.167278	-0.176434	0.881755
50	6	C	-4.626608	0.127490	-0.249191
51	6	C	-5.646427	0.426601	-1.106769
52	6	C	-6.928704	0.186733	-0.522276
53	6	C	-6.856922	-0.285774	0.756682
54	16	S	-5.209354	-0.452337	1.287081
55	1	H	-5.489810	0.800783	-2.108901
56	1	H	-7.863160	0.361347	-1.039145
57	1	H	-7.663493	-0.547734	1.424866
58	35	Br	-2.756546	0.291065	-0.591772

E(RB3LYP) = –4317.21280396 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.471164
Thermal correction to Energy = 0.488200
Thermal correction to Enthalpy 0.488818
Thermal correction to Gibbs Free Energy = 0.430811
Sum of electronic and zero-point Energies = -4316.741640
Sum of electronic and thermal Energies = -4316.724604
Sum of electronic and thermal Enthalpies = -4316.723986
Sum of electronic and thermal Free Energies = -4316.781993

Table C22. Cartesian coordinates and energies for Adduct **Add-2b (Cl)** found in Figure C4 and Figure 5.14. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-1.342315	1.305845	-0.652997
2	6	C	-6.126928	-0.487911	-0.827332
3	1	H	-6.158461	0.077273	-1.765387
4	1	H	-7.159621	-0.652809	-0.504234
5	1	H	-5.687230	-1.466676	-1.048450
6	6	C	-5.305542	0.254732	0.232942
7	1	H	-5.776518	1.219642	0.459691
8	1	H	-5.309414	-0.314397	1.171356
9	6	C	-3.842849	0.504914	-0.180066
10	1	H	-3.868212	1.055281	-1.136914
11	1	H	-3.402566	-0.474468	-0.426128
12	6	C	-2.951314	1.248246	0.836405
13	1	H	-3.005007	0.670837	1.783525
14	1	H	-3.459727	2.201592	1.080303
15	3	Li	-0.977886	1.657343	1.602392
16	6	C	0.843870	3.334734	-0.016590
17	6	C	0.592094	1.986929	0.083106
18	6	C	1.860667	1.286538	-0.003557
19	6	C	2.973487	2.069871	-0.158194
20	16	S	2.555218	3.754001	-0.211099
21	1	H	1.945462	0.206770	0.046001
22	1	H	4.007514	1.764753	-0.245115
23	1	H	0.146626	4.164883	0.005887
24	6	C	1.565080	-2.416773	1.054985
25	6	C	0.682503	-2.244057	0.030149
26	6	C	1.274718	-2.257051	-1.267541
27	6	C	2.624810	-2.440374	-1.198476
28	16	S	3.174555	-2.598631	0.439188
29	1	H	0.718768	-2.128982	-2.185148
30	1	H	3.333128	-2.488338	-2.011379
31	1	H	1.366482	-2.437829	2.114500
32	17	Cl	-1.032386	-1.988930	0.273464

E(RB3LYP) = –1738.19236572 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.233669
Thermal correction to Energy = 0.244327
Thermal correction to Enthalpy 0.244945
Thermal correction to Gibbs Free Energy = 0.203033
Sum of electronic and zero-point Energies = -1737.958697
Sum of electronic and thermal Energies = -1737.948039
Sum of electronic and thermal Enthalpies = -1737.947241
Sum of electronic and thermal Free Energies = -1737.989333

Table C23. Cartesian coordinates and energies for Adduct **Add-2b (Br)** found in Figure C4 and Figure 5.14. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	1.184322	1.876022	-1.159982
2	6	C	6.099932	-0.707932	-0.023527
3	1	H	5.835025	-1.289172	0.866688
4	1	H	7.187807	-0.586481	-0.029398
5	1	H	5.827497	-1.308083	-0.898765
6	6	C	5.370174	0.640515	-0.034668
7	1	H	5.678143	1.235378	0.835129
8	1	H	5.671667	1.217730	-0.918517
9	6	C	3.835926	0.514838	-0.027381
10	1	H	3.559546	-0.091308	0.850255
11	1	H	3.551496	-0.103461	-0.893959
12	6	C	3.029050	1.829358	-0.032715
13	1	H	3.378320	2.426702	-0.901337
14	1	H	3.386137	2.437289	0.825445
15	3	Li	1.210574	1.863440	1.140447
16	6	C	-1.703120	1.594705	-0.007064
17	6	C	-0.597754	2.410260	0.009722
18	6	C	-1.059575	3.788303	0.014944
19	6	C	-2.417514	3.972980	0.003287
20	16	S	-3.252985	2.451625	-0.015369
21	1	H	-0.385771	4.641338	0.026927
22	1	H	-2.974863	4.899903	0.004302
23	1	H	-1.754131	0.514620	-0.016968
24	6	C	-1.668230	-2.149668	-1.041817
25	6	C	-0.911166	-1.944799	0.073660
26	6	C	-1.635579	-2.030468	1.300834
27	6	C	-2.955384	-2.301182	1.084749
28	16	S	-3.317867	-2.453941	-0.604886
29	1	H	-1.192111	-1.887469	2.275643
30	1	H	-3.739868	-2.419034	1.816749
31	1	H	-1.364150	-2.123257	-2.075884
32	35	Br	0.941818	-1.498500	0.008463

E(RB3LYP) = –3852.11619671 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction =	0.232791
Thermal correction to Energy =	0.243606
Thermal correction to Enthalpy	0.244224
Thermal correction to Gibbs Free Energy =	0.201160
Sum of electronic and zero-point Energies =	-3851.883405
Sum of electronic and thermal Energies =	-3851.872591
Sum of electronic and thermal Enthalpies =	-3851.871973
Sum of electronic and thermal Free Energies =	-3851.915037

Table C24. Cartesian coordinates and energies for Adduct **Add-4b (Cl)** found in Figure C4 and Figure 5.15. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-0.287873	-1.002291	-1.083132
2	6	C	-5.458765	0.411106	-0.672576
3	1	H	-5.468136	-0.567803	-0.180337
4	1	H	-6.428752	0.547068	-1.161415
5	1	H	-5.372141	1.170295	0.112772
6	6	C	-4.292414	0.514315	-1.662435
7	1	H	-4.409909	-0.235987	-2.455204
8	1	H	-4.315710	1.490694	-2.163717
9	6	C	-2.912829	0.328225	-1.007087
10	1	H	-2.920054	-0.642673	-0.488967
11	1	H	-2.832733	1.064520	-0.192744
12	6	C	-1.676554	0.423357	-1.924273
13	1	H	-1.706202	1.398737	-2.444871
14	1	H	-1.805357	-0.303378	-2.748926
15	3	Li	-0.216545	1.254198	-0.551718
16	6	C	-0.730670	3.190561	1.624744
17	8	O	-0.746530	2.965186	0.199640
18	6	C	-1.824913	3.767828	-0.334100
19	6	C	-2.893611	3.848120	0.779274
20	6	C	-2.207906	3.208446	2.012416
21	1	H	-0.155312	2.384167	2.077938
22	1	H	-0.244766	4.152638	1.831425
23	1	H	-1.431719	4.758355	-0.586015
24	1	H	-2.172813	3.279454	-1.243291
25	1	H	-3.170797	4.886424	0.969053
26	1	H	-3.798345	3.305911	0.502025
27	1	H	-2.387251	3.764840	2.933563
28	1	H	-2.558807	2.184887	2.158256
29	6	C	-2.250917	-3.213419	-1.586076
30	8	O	-1.027808	-2.799972	-0.932668
31	6	C	-0.961536	-3.519241	0.318832
32	6	C	-2.396211	-3.479936	0.835665
33	6	C	-3.241089	-3.581910	-0.457247
34	1	H	-2.583583	-2.382693	-2.207157
35	1	H	-2.031515	-4.074423	-2.226104
36	1	H	-0.626106	-4.546129	0.124655
37	1	H	-0.240610	-3.010241	0.956269
38	1	H	-2.605655	-4.282789	1.544338
39	1	H	-2.567915	-2.525177	1.336193
40	1	H	-3.626267	-4.592788	-0.602795
41	1	H	-4.092258	-2.900188	-0.434110
42	6	C	1.600176	-0.802855	1.271756
43	6	C	0.407390	-0.251656	0.881948
44	6	C	-0.540850	-0.418648	1.970860
45	6	C	-0.072537	-1.049728	3.092443
46	16	S	1.593192	-1.504272	2.903524
47	1	H	-1.572230	-0.082396	1.913314
48	1	H	-0.598164	-1.281492	4.008986
49	1	H	2.533658	-0.863463	0.728491

50	6	C	4.324153	-0.584343	-1.396975
51	6	C	3.521490	0.509306	-1.532893
52	6	C	3.754914	1.537376	-0.572518
53	6	C	4.752502	1.195316	0.292162
54	16	S	5.406451	-0.373223	-0.059359
55	1	H	3.197261	2.461906	-0.532303
56	1	H	5.138347	1.764890	1.123707
57	1	H	4.336774	-1.484393	-1.990443
58	17	Cl	2.284224	0.642964	-2.764940

E(RB3LYP) = –2203.29640307 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.471275		
Thermal correction to Energy =		0.488157		
Thermal correction to Enthalpy		0.488775		
Thermal correction to Gibbs Free Energy =		0.432225		
Sum of electronic and zero-point Energies =		-2202.825128		
Sum of electronic and thermal Energies =		-2202.808246		
Sum of electronic and thermal Enthalpies =		-2202.807628		
Sum of electronic and thermal Free Energies =		-2202.864178		

Table C25. Cartesian coordinates and energies for Adduct **Add-4b (Br)** found in Figure C4 and Figure 5.15. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	0.332258	1.060876	0.524897
2	6	C	3.801334	1.164043	-3.419016
3	1	H	4.205016	1.905461	-2.720589
4	1	H	4.073770	1.477793	-4.431583
5	1	H	4.309676	0.214975	-3.216090
6	6	C	2.284597	1.020216	-3.247639
7	1	H	1.791693	1.972570	-3.481937
8	1	H	1.895607	0.291486	-3.970294
9	6	C	1.868614	0.584171	-1.832151
10	1	H	2.296369	1.311181	-1.126072
11	1	H	2.398758	-0.352520	-1.606091
12	6	C	0.356700	0.416332	-1.570168
13	1	H	-0.042103	-0.307761	-2.302723
14	1	H	-0.148695	1.358185	-1.844595
15	3	Li	0.418341	-1.206357	-0.132463
16	6	C	2.344800	-3.441490	-0.000135
17	8	O	1.299113	-2.817065	-0.776850
18	6	C	1.630820	-3.033401	-2.168465
19	6	C	3.173829	-3.103637	-2.238057
20	6	C	3.621539	-3.085201	-0.755604
21	1	H	2.294332	-3.035035	1.008782
22	1	H	2.174132	-4.525195	0.024918
23	1	H	1.169762	-3.970774	-2.496409

24	1	H	1.202994	-2.207951	-2.736337
25	1	H	3.491933	-4.019275	-2.739585
26	1	H	3.587095	-2.259157	-2.790883
27	1	H	4.435138	-3.782055	-0.548820
28	1	H	3.943269	-2.084004	-0.461848
29	6	C	1.200181	3.801786	-0.351139
30	8	O	1.046774	2.861506	0.737578
31	6	C	2.077541	3.169827	1.699714
32	6	C	3.304688	3.461704	0.840343
33	6	C	2.705722	4.147144	-0.412764
34	1	H	0.823557	3.319130	-1.251891
35	1	H	0.592171	4.686898	-0.137406
36	1	H	1.773093	4.046441	2.285550
37	1	H	2.182639	2.306096	2.354654
38	1	H	4.034518	4.086342	1.357507
39	1	H	3.790070	2.521688	0.569566
40	1	H	2.851002	5.228311	-0.383350
41	1	H	3.163557	3.773491	-1.329353
42	6	C	2.607706	-0.365971	1.675017
43	6	C	1.243249	-0.483213	1.773223
44	6	C	0.937750	-1.105300	3.047131
45	6	C	2.011315	-1.430183	3.835302
46	16	S	3.506170	-0.987685	3.069562
47	1	H	-0.075641	-1.315337	3.378485
48	1	H	2.019252	-1.894380	4.812211
49	1	H	3.200011	0.036598	0.862540
50	6	C	-5.599415	-0.049563	-0.947885
51	6	C	-4.577005	-0.046574	-0.045871
52	6	C	-4.999394	-0.144233	1.315035
53	6	C	-6.358140	-0.220260	1.418462
54	16	S	-7.128492	-0.174249	-0.135828
55	1	H	-4.321823	-0.155682	2.157045
56	1	H	-6.955273	-0.301016	2.314192
57	1	H	-5.548025	0.013511	-2.023268
58	35	Br	-2.728234	0.079848	-0.543462

E(RB3LYP) = –4317.21617349 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =	0.470682			
Thermal correction to Energy =	0.487875			
Thermal correction to Enthalpy	0.488493			
Thermal correction to Gibbs Free Energy =	0.429445			
Sum of electronic and zero-point Energies =	-4316.745492			
Sum of electronic and thermal Energies =	-4316.728298			
Sum of electronic and thermal Enthalpies =	-4316.727680			
Sum of electronic and thermal Free Energies =	-4316.786728			

Table C26. Cartesian coordinates and energies for Adduct **Add-2c (Cl)** found in Figure C4 and Figure 5.18. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	1.115896	1.300717	1.138838
2	6	C	6.060426	-1.152667	0.017454
3	1	H	5.787364	-1.760819	0.886979
4	1	H	7.146412	-1.016035	0.035463
5	1	H	5.813124	-1.733141	-0.878295
6	6	C	5.312080	0.185546	0.027945
7	1	H	5.595244	0.760469	0.919384
8	1	H	5.623738	0.790627	-0.833532
9	6	C	3.779811	0.041342	0.001079
10	1	H	3.491056	-0.595297	0.852123
11	1	H	3.517564	-0.552673	-0.888926
12	6	C	2.961676	1.348410	0.020190
13	1	H	3.327414	1.976816	-0.819510
14	1	H	3.291533	1.932114	0.905638
15	3	Li	1.170591	1.493492	-1.170666
16	6	C	-0.635151	2.013783	-0.021166
17	6	C	-1.876401	1.397894	-0.103343
18	6	C	-3.028375	2.251880	-0.107209
19	6	C	-2.703357	3.578020	-0.025635
20	16	S	-0.972480	3.750491	0.056979
21	1	H	-1.973699	0.318980	-0.160575
22	1	H	-4.049978	1.892829	-0.168106
23	1	H	-3.366109	4.431907	-0.009603
24	6	C	-1.690498	-2.346731	-1.030538
25	6	C	-0.836385	-2.137947	0.011437
26	6	C	-1.458347	-2.149179	1.295215
27	6	C	-2.801627	-2.366457	1.198169
28	16	S	-3.309003	-2.559565	-0.449536
29	1	H	-0.926806	-1.996800	2.223589
30	1	H	-3.526886	-2.422974	1.995483
31	1	H	-1.467818	-2.372304	-2.085143
32	17	Cl	0.874059	-1.827911	-0.194127

E(RB3LYP) = –1738.20628361 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.233780		
Thermal correction to Energy =		0.244363		
Thermal correction to Enthalpy		0.244981		
Thermal correction to Gibbs Free Energy =		0.203245		
Sum of electronic and zero-point Energies =		-1737.972503		
Sum of electronic and thermal Energies =		-1737.961921		
Sum of electronic and thermal Enthalpies =		-1737.961303		
Sum of electronic and thermal Free Energies =		-1738.003039		

Table C27. Cartesian coordinates and energies for Adduct **Add-2c (Br)** found in Figure C4 and Figure 5.18. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	-5.507330	-2.183754	0.868196
2	1	H	-4.736513	-2.822144	1.313721
3	1	H	-6.300745	-2.835595	0.489245
4	1	H	-5.933816	-1.574094	1.672454
5	6	C	-4.915570	-1.298968	-0.235004
6	1	H	-4.517019	-1.927514	-1.041542
7	1	H	-5.707534	-0.688361	-0.686864
8	6	C	-3.794022	-0.364832	0.255821
9	1	H	-3.025611	-0.997380	0.728427
10	1	H	-4.212281	0.236420	1.080972
11	6	C	-3.154140	0.560724	-0.801966
12	1	H	-3.973945	1.152179	-1.254110
13	1	H	-2.821898	-0.097951	-1.632022
14	3	Li	-2.026803	1.627525	0.738120
15	3	Li	-1.384306	1.589864	-1.505907
16	6	C	-0.215451	2.643810	0.030724
17	6	C	1.051376	2.217047	0.406806
18	16	S	-0.119042	4.405068	-0.053819
19	6	C	2.043353	3.231788	0.616152
20	1	H	1.284248	1.164318	0.535042
21	6	C	1.559962	4.493271	0.402099
22	1	H	3.067263	3.029457	0.910956
23	1	H	2.083148	5.435600	0.485341
24	6	C	2.576789	-1.063166	-0.700357
25	6	C	1.613903	-1.802776	-0.079509
26	6	C	2.118380	-2.857897	0.739195
27	6	C	3.482405	-2.896135	0.722132
28	16	S	4.153094	-1.653058	-0.286136
29	1	H	1.494171	-3.538508	1.300197
30	1	H	4.136359	-3.580509	1.240981
31	1	H	2.456226	-0.215059	-1.354740
32	35	Br	-0.250328	-1.442853	-0.268319

E(RB3LYP) = –3852.12640951 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction =	0.233558
Thermal correction to Energy =	0.244289
Thermal correction to Enthalpy	0.244907
Thermal correction to Gibbs Free Energy =	0.201649
Sum of electronic and zero-point Energies =	-3851.892852
Sum of electronic and thermal Energies =	-3851.882120
Sum of electronic and thermal Enthalpies =	-3851.881502
Sum of electronic and thermal Free Energies =	-3851.924761

Table C28. Cartesian coordinates and energies for Adduct **Add-4c (Cl)** found in Figure C4 and Figure 5.19. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-1.201627	-1.400931	-0.950119
2	6	C	-4.635257	2.671980	-0.559374
3	1	H	-5.147097	1.884889	0.005420
4	1	H	-5.401649	3.296267	-1.029642
5	1	H	-4.096196	3.293830	0.163803
6	6	C	-3.671143	2.068274	-1.587258
7	1	H	-4.233661	1.476661	-2.321470
8	1	H	-3.182734	2.870645	-2.155418
9	6	C	-2.586636	1.174820	-0.960193
10	1	H	-3.098841	0.397650	-0.372599
11	1	H	-2.062078	1.777976	-0.202326
12	6	C	-1.566518	0.525578	-1.918405
13	1	H	-1.072624	1.333688	-2.491325
14	1	H	-2.123312	-0.028102	-2.695909
15	3	Li	0.181170	0.475562	-0.705948
16	6	C	1.318602	2.294847	1.297235
17	8	O	0.855808	2.160979	-0.065209
18	6	C	0.310549	3.445982	-0.437899
19	6	C	-0.313606	4.028947	0.847414
20	6	C	0.228500	3.119209	1.981498
21	1	H	1.451581	1.293372	1.703614
22	1	H	2.283291	2.818279	1.292167
23	1	H	1.126480	4.075722	-0.809454
24	1	H	-0.404204	3.276712	-1.242442
25	1	H	-0.015459	5.070062	0.981437
26	1	H	-1.403155	3.996434	0.806030
27	1	H	0.616658	3.685949	2.829196
28	1	H	-0.552374	2.449914	2.345252
29	6	C	-4.108301	-2.059866	-1.396419
30	8	O	-2.871234	-2.396751	-0.725823
31	6	C	-3.238154	-2.967193	0.547667
32	6	C	-4.379863	-2.076398	1.029474
33	6	C	-5.124881	-1.722497	-0.281076
34	1	H	-3.898467	-1.227288	-2.065863
35	1	H	-4.431354	-2.923316	-1.987411
36	1	H	-3.565869	-4.003881	0.397426
37	1	H	-2.354553	-2.950807	1.183984
38	1	H	-5.018156	-2.576352	1.759557
39	1	H	-3.965371	-1.178538	1.493184
40	1	H	-6.031177	-2.319349	-0.397106
41	1	H	-5.411330	-0.670540	-0.306821
42	6	C	0.087733	-1.138918	0.806140
43	6	C	1.355842	-1.525965	1.214720
44	6	C	1.640936	-1.452799	2.618932
45	6	C	0.577516	-0.998282	3.349887
46	16	S	-0.762295	-0.666528	2.285978
47	1	H	2.109512	-1.850749	0.504215
48	1	H	2.594678	-1.722371	3.059508
49	1	H	0.512262	-0.851651	4.419024

50	6	C	4.296020	-1.628650	-1.186928
51	6	C	3.513679	-0.593168	-1.604744
52	6	C	3.651688	0.601481	-0.838844
53	6	C	4.552372	0.442200	0.172653
54	16	S	5.233221	-1.153737	0.191151
55	1	H	3.081168	1.500699	-1.018315
56	1	H	4.849911	1.162726	0.918954
57	1	H	4.363216	-2.625098	-1.593213
58	17	Cl	2.392729	-0.717906	-2.945762

E(RB3LYP) = –2203.31012602 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.472615	
Thermal correction to Energy =	0.489060	
Thermal correction to Enthalpy	0.489678	
Thermal correction to Gibbs Free Energy =	0.435173	
Sum of electronic and zero-point Energies =	-2202.837511	
Sum of electronic and thermal Energies =	-2202.821066	
Sum of electronic and thermal Enthalpies =	-2202.820448	
Sum of electronic and thermal Free Energies =	-2202.874953	

Table C29. Cartesian coordinates and energies for Adduct **Add-4c (Br)** found in Figure C4 and Figure 5.19. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-4.272855	0.999240	-3.099165
2	1	H	-4.615809	-0.028037	-2.933645
3	1	H	-4.669801	1.331537	-4.063522
4	1	H	-4.724876	1.622673	-2.319976
5	6	C	-2.742870	1.079685	-3.046637
6	1	H	-2.310030	0.464989	-3.846122
7	1	H	-2.416621	2.108796	-3.244859
8	6	C	-2.152136	0.625355	-1.700479
9	1	H	-2.530965	-0.388901	-1.501758
10	1	H	-2.615784	1.238429	-0.913098
11	6	C	-0.614353	0.655445	-1.567258
12	1	H	-0.260169	1.673766	-1.802073
13	1	H	-0.185471	0.041703	-2.379224
14	3	Li	-0.486612	1.192304	0.546263
15	3	Li	-0.416877	-1.037071	-0.268608
16	6	C	-1.527846	-2.941785	-2.257167
17	8	O	-1.057725	-2.736467	-0.904104
18	6	C	-1.880081	-3.567190	-0.053602
19	6	C	-3.285544	-3.388856	-0.621324
20	6	C	-3.039394	-3.244453	-2.144255
21	1	H	-1.299167	-2.038521	-2.821875
22	1	H	-0.979789	-3.783778	-2.692304
23	1	H	-1.536917	-4.606453	-0.132558

24	1	H	-1.756947	-3.219572	0.971187
25	1	H	-3.941413	-4.225429	-0.375430
26	1	H	-3.723373	-2.476373	-0.212243
27	1	H	-3.285703	-4.163255	-2.679166
28	1	H	-3.639951	-2.439368	-2.569306
29	6	C	-2.254475	3.066726	2.020149
30	8	O	-1.352149	2.910267	0.904535
31	6	C	-1.813137	3.820729	-0.121319
32	6	C	-3.347012	3.914369	0.047122
33	6	C	-3.630620	3.152196	1.365761
34	1	H	-2.120703	2.208729	2.677385
35	1	H	-2.001980	3.987838	2.560748
36	1	H	-1.331486	4.791923	0.032958
37	1	H	-1.499425	3.415577	-1.081948
38	1	H	-3.661042	4.957452	0.112898
39	1	H	-3.869366	3.460980	-0.795941
40	1	H	-4.361589	3.656824	1.999269
41	1	H	-3.994640	2.143650	1.158367
42	6	C	-0.960512	-0.529579	1.803459
43	6	C	-0.267157	-1.377753	2.655093
44	6	C	-1.041648	-2.135429	3.596533
45	6	C	-2.382609	-1.885713	3.494891
46	16	S	-2.664566	-0.717745	2.232625
47	1	H	0.815401	-1.471015	2.610486
48	1	H	-0.618875	-2.831321	4.312940
49	1	H	-3.189121	-2.306977	4.078573
50	6	C	4.972316	0.008472	0.910683
51	6	C	4.484369	0.226469	-0.343669
52	6	C	5.488715	0.306199	-1.355883
53	6	C	6.740955	0.144223	-0.837694
54	16	S	6.703465	-0.105529	0.879206
55	1	H	5.278208	0.474227	-2.402532
56	1	H	7.685690	0.156112	-1.359993
57	1	H	4.427404	-0.091094	1.836036
58	35	Br	2.613050	0.402316	-0.723441

E(RB3LYP) = –4317.22841717 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.471180

Thermal correction to Energy = 0.488257

Thermal correction to Enthalpy 0.488875

Thermal correction to Gibbs Free Energy = 0.430620

Sum of electronic and zero-point Energies = -4316.757237

Sum of electronic and thermal Energies = -4316.740160

Sum of electronic and thermal Enthalpies = -4316.739542

Sum of electronic and thermal Free Energies = -4316.797797

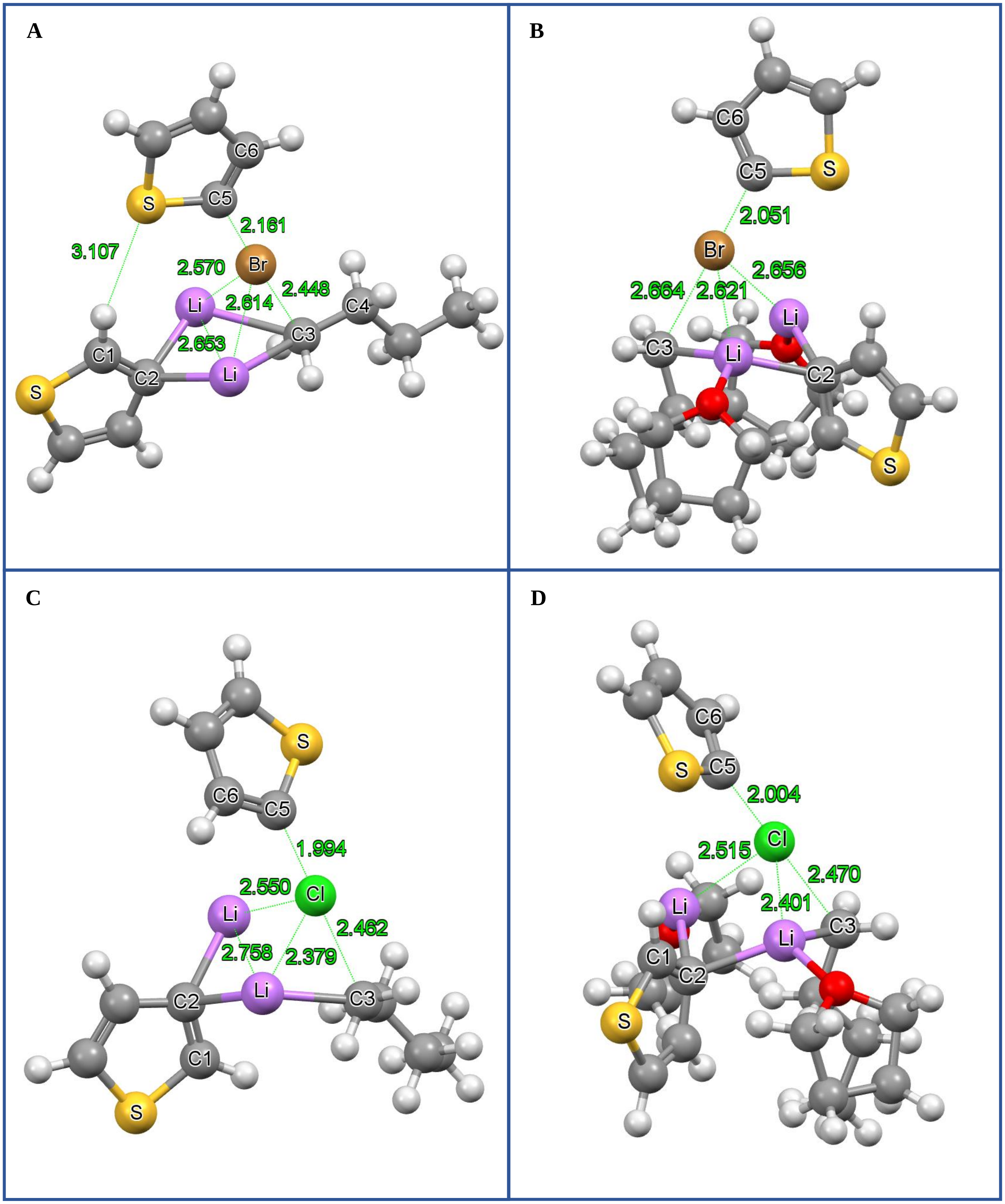


Figure C5. Optimised transition structures **TS–2D** and **TS–4D** for the reactions: **Prod–1b+** 2-Br-thiophene → **Prod–2d** (A), **Prod–2b +** 2-Br-thiophene → **Prod–4d** (B), **Prod–1b +** 2-Cl-thiophene → **Prod–2d** (C) and **Prod–2b +** 2-Cl-thiophene → **Prod–4d** (D)

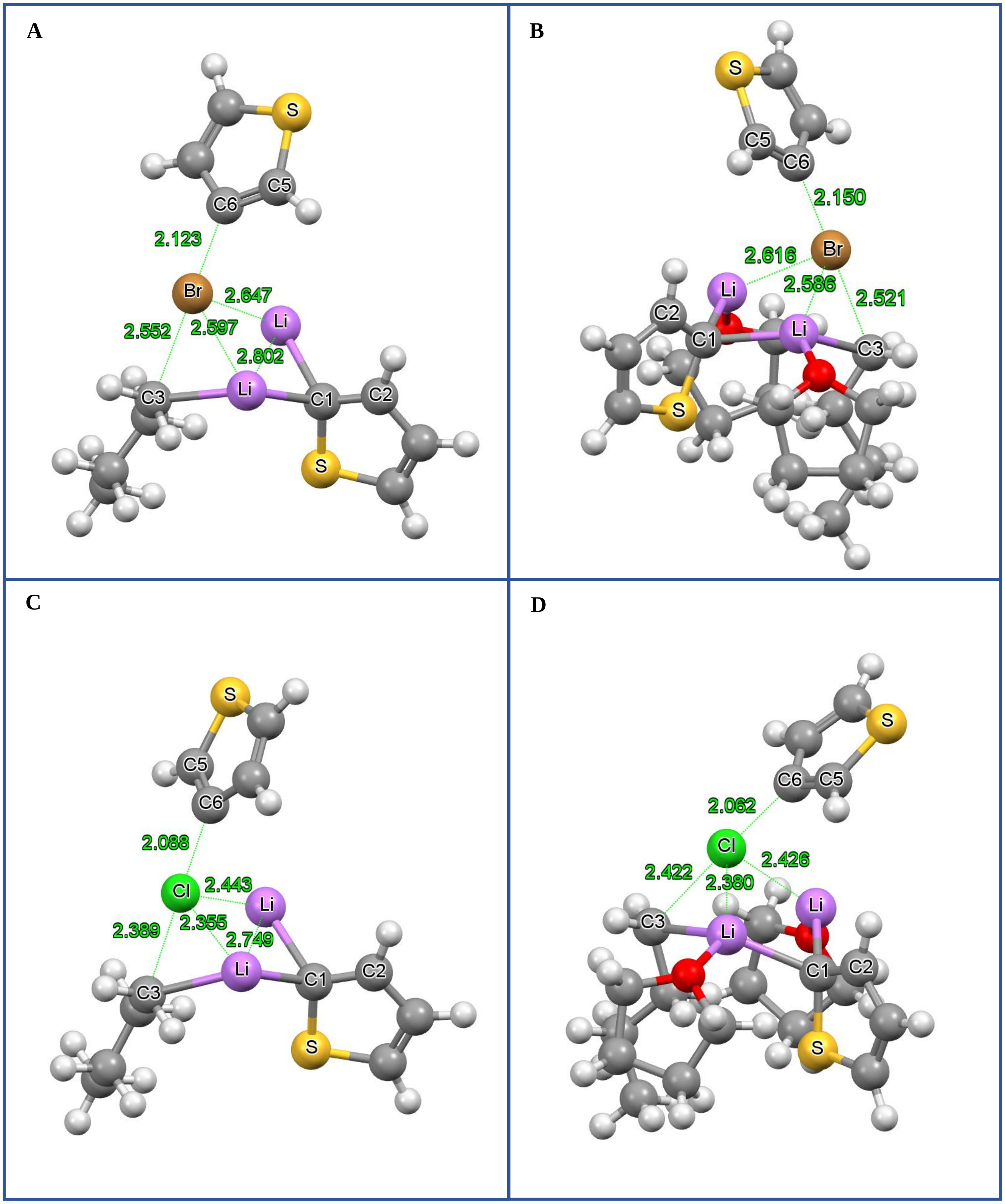


Figure C6. Optimised transition structures **TS–2C** and **TS–4C** for the reactions: **Prod–1a+** 3-Br-thiophene → **Prod–2c** (A), **Prod–2a +** 3-Br-thiophene → **Prod–4c** (B), **Prod–1a +** 3-Cl-thiophene → **Prod–2c** (C) and **Prod–2a +** 3-Cl-thiophene → **Prod–4c** (D)

Table C30. Cartesian coordinates and energies for Transition state **TS–1A (Cl)** found in Figure 5.3 and Figure 5.4. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	-3.550994	3.156697	-1.259396
2	1	H	-2.843894	3.810897	-1.780796
3	1	H	-4.495494	3.700097	-1.158396
4	1	H	-3.733093	2.288697	-1.902396
5	6	C	-2.993794	2.720197	0.100504
6	1	H	-2.844294	3.597797	0.741404
7	1	H	-3.728193	2.086797	0.613404
8	6	C	-1.665093	1.948798	-0.008796
9	1	H	-0.936294	2.585098	-0.530596
10	1	H	-1.836093	1.089997	-0.673996
11	6	C	-1.061093	1.476798	1.304104
12	1	H	-1.775593	0.855697	1.872604
13	1	H	-0.774793	2.309698	1.952304
14	3	Li	-0.043593	-1.492002	-1.336796
15	6	C	-5.464693	-1.940903	-0.209096
16	1	H	-5.621893	-1.078403	0.447504
17	1	H	-6.284193	-2.645503	-0.035996
18	1	H	-5.544093	-1.584803	-1.241996
19	6	C	-4.094693	-2.579903	0.046604
20	1	H	-4.048093	-2.955603	1.076904
21	1	H	-3.966593	-3.456103	-0.602096
22	6	C	-2.916593	-1.617103	-0.180496
23	1	H	-3.082293	-0.732303	0.452104
24	1	H	-2.990393	-1.232903	-1.209696
25	6	C	-1.504593	-2.193802	0.068604
26	1	H	-1.399493	-3.099502	-0.560096
27	1	H	-1.496693	-2.623902	1.090604
28	3	Li	-0.491593	-0.708102	1.214304
29	6	C	3.063007	0.284298	0.148104
30	6	C	4.092807	1.114098	-0.193696
31	6	C	5.273907	0.411598	-0.609096
32	6	C	5.130007	-0.946302	-0.583296
33	16	S	3.529607	-1.384002	-0.035796
34	1	H	4.019507	2.194298	-0.152796
35	1	H	6.191207	0.902399	-0.912296
36	1	H	5.854107	-1.706601	-0.837496
37	17	Cl	1.212907	0.790098	0.738104

E(RB3LYP) = –1343.57337300 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm

Zero-point correction = 0.297066
Thermal correction to Energy = 0.307906
Thermal correction to Enthalpy 0.308524
Thermal correction to Gibbs Free Energy = 0.266623
Sum of electronic and zero-point Energies = -1343.276307
Sum of electronic and thermal Energies = -1343.265467
Sum of electronic and thermal Enthalpies = -1343.264849
Sum of electronic and thermal Free Energies = -1343.306750

Table C31. Cartesian coordinates and energies for Transition state **TS–1A (Br)** found in Figure 5.3 and Figure 5.4. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	-6.261991	-0.283282	-0.619102
2	1	H	-6.087192	-0.435483	-1.689402
3	1	H	-7.263190	0.142120	-0.501802
4	1	H	-6.259593	-1.268682	-0.141602
5	6	C	-5.185889	0.623015	-0.011202
6	1	H	-5.226887	1.612616	-0.483402
7	1	H	-5.395289	0.783916	1.053498
8	6	C	-3.763191	0.056412	-0.159102
9	1	H	-3.565991	-0.113688	-1.226902
10	1	H	-3.732493	-0.937688	0.305398
11	6	C	-2.660189	0.924910	0.433098
12	1	H	-2.812788	1.046510	1.514998
13	1	H	-2.702186	1.936310	-0.006002
14	3	Li	-0.832887	1.836806	-0.922902
15	6	C	4.389316	2.865594	-0.368102
16	1	H	4.650314	2.254394	0.502598
17	1	H	5.180717	3.609593	-0.503102
18	1	H	4.397214	2.206494	-1.242902
19	6	C	3.013317	3.516997	-0.186402
20	1	H	3.032319	4.190497	0.680198
21	1	H	2.783218	4.147298	-1.055302
22	6	C	1.873015	2.501500	0.002198
23	1	H	2.138213	1.857599	0.855698
24	1	H	1.890313	1.818000	-0.861502
25	6	C	0.453916	3.081603	0.195598
26	1	H	0.250018	3.761103	-0.656502
27	1	H	0.490318	3.782203	1.052198
28	3	Li	-0.536687	1.802205	1.578698
29	6	C	1.012305	-1.844698	0.029998
30	6	C	0.963602	-3.213298	0.046398
31	6	C	2.250901	-3.840101	-0.042302
32	6	C	3.277003	-2.941503	-0.124802
33	16	S	2.666706	-1.306302	-0.093902
34	1	H	0.034601	-3.766796	0.121998
35	1	H	2.401298	-4.913401	-0.044002
36	1	H	4.337002	-3.136206	-0.201202
37	35	Br	-0.664892	-0.493595	0.196698

E(RB3LYP) = –3457.50839273 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.297930

Thermal correction to Energy = 0.308762

Thermal correction to Enthalpy 0.309380

Thermal correction to Gibbs Free Energy = 0.268212

Sum of electronic and zero-point Energies = -3457.210463

Sum of electronic and thermal Energies = -3457.199631

Sum of electronic and thermal Enthalpies = -3457.199013

Sum of electronic and thermal Free Energies = -3457.240181

Table C32. Cartesian coordinates and energies for Transition state **TS–3A (Cl)** found in Figure 5.5 and Figure 5.6. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-3.135336	2.736651	-1.830240
2	1	H	-3.784394	2.163132	-1.159683
3	1	H	-3.776561	3.312338	-2.504578
4	1	H	-2.575510	3.447991	-1.213715
5	6	C	-2.184775	1.809949	-2.596635
6	1	H	-2.762082	1.125538	-3.230148
7	1	H	-1.557071	2.397514	-3.277473
8	6	C	-1.268228	0.987377	-1.668066
9	1	H	-1.924024	0.451474	-0.966192
10	1	H	-0.714333	1.692523	-1.038691
11	6	C	-0.291120	0.043263	-2.362759
12	1	H	0.340862	0.595950	-3.062722
13	1	H	-0.798074	-0.748324	-2.930502
14	3	Li	1.237547	0.104660	0.855766
15	6	C	-3.847255	0.383578	3.399151
16	1	H	-3.647341	1.460500	3.416608
17	1	H	-4.359566	0.124405	4.331029
18	1	H	-4.543067	0.195588	2.573965
19	6	C	-2.548604	-0.410299	3.214829
20	1	H	-1.874972	-0.221348	4.060493
21	1	H	-2.765841	-1.486362	3.236844
22	6	C	-1.808855	-0.081765	1.906694
23	1	H	-1.640108	1.005171	1.879331
24	1	H	-2.508620	-0.268578	1.079606
25	6	C	-0.480143	-0.821802	1.656656
26	1	H	-0.662473	-1.906383	1.775964
27	1	H	0.171657	-0.605515	2.529881
28	3	Li	-0.564180	-1.222369	-0.496701
29	6	C	-3.253052	-1.953062	-1.813203
30	8	O	-2.245891	-2.254929	-0.824994
31	6	C	-2.929967	-3.013887	0.199429
32	6	C	-4.355129	-2.426645	0.282128
33	6	C	-4.472141	-1.544235	-0.987305
34	1	H	-2.866807	-1.173542	-2.465472
35	1	H	-3.450399	-2.853886	-2.407968
36	1	H	-2.947686	-4.066773	-0.102863
37	1	H	-2.358534	-2.914913	1.119594
38	1	H	-5.100269	-3.223700	0.292385
39	1	H	-4.485521	-1.834673	1.188302
40	1	H	-5.406436	-1.698942	-1.528985
41	1	H	-4.400831	-0.485959	-0.727197
42	6	C	0.852938	2.857860	1.831028
43	8	O	1.465945	2.003283	0.843694
44	6	C	1.730124	2.807623	-0.335694
45	6	C	0.750895	4.002251	-0.272630
46	6	C	-0.066596	3.758601	1.015615
47	1	H	0.338734	2.218497	2.548918
48	1	H	1.631221	3.431609	2.349209
49	1	H	2.774145	3.132667	-0.309299

50	1	H	1.580611	2.161965	-1.200014
51	1	H	1.301524	4.942609	-0.210988
52	1	H	0.112323	4.045923	-1.155839
53	1	H	-0.318936	4.682269	1.538439
54	1	H	-0.992543	3.224805	0.791688
55	6	C	3.508475	-1.323209	-0.441323
56	6	C	3.734339	-2.503911	0.208989
57	6	C	5.021381	-2.561324	0.837904
58	6	C	5.752071	-1.419144	0.668280
59	16	S	4.867480	-0.248353	-0.275964
60	1	H	3.009024	-3.307703	0.241807
61	1	H	5.383817	-3.418953	1.391644
62	1	H	6.745989	-1.196607	1.028548
63	17	Cl	1.818692	-0.766328	-1.30414

E(RB3LYP) = –1808.67503953 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.535151		
Thermal correction to Energy =		0.552237		
Thermal correction to Enthalpy		0.552855		
Thermal correction to Gibbs Free Energy =		0.497270		
Sum of electronic and zero-point Energies =		-1808.139888		
Sum of electronic and thermal Energies =		-1808.122802		
Sum of electronic and thermal Enthalpies =		-1808.122184		
Sum of electronic and thermal Free Energies =		-1808.177770		

Table C33. Cartesian coordinates and energies for Transition state **TS–3A (Br)** found in Figure 5.5 and Figure 5.6. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	4.214104	-0.499201	3.272601
2	1	H	4.631804	-1.232901	2.574201
3	1	H	4.625204	-0.713201	4.264201
4	1	H	4.578603	0.487399	2.966201
5	6	C	2.681704	-0.544403	3.261901
6	1	H	2.337905	-1.530303	3.601801
7	1	H	2.283403	0.179597	3.984701
8	6	C	2.068903	-0.255504	1.881501
9	1	H	2.505404	-0.972703	1.171301
10	1	H	2.448202	0.718397	1.540301
11	6	C	0.531203	-0.282005	1.782201
12	1	H	0.145403	0.427594	2.544601
13	1	H	0.182104	-1.256205	2.177001
14	3	Li	-0.524598	1.182294	0.664601
15	6	C	4.098502	0.976499	-2.171299
16	1	H	4.126601	1.819799	-1.473499
17	1	H	4.806502	1.187699	-2.978299
18	1	H	4.460303	0.095199	-1.630999
19	6	C	2.678402	0.749197	-2.702299
20	1	H	2.342701	1.631597	-3.260999
21	1	H	2.677303	-0.082803	-3.417199

22	6	C	1.660003	0.450296	-1.585599
23	1	H	1.684002	1.280796	-0.872099
24	1	H	2.051103	-0.406104	-1.019899
25	6	C	0.226303	0.203495	-2.068899
26	1	H	0.193104	-0.634905	-2.777699
27	1	H	-0.133498	1.084594	-2.610299
28	3	Li	0.154704	-1.104405	-0.172799
29	6	C	1.625907	-3.603804	0.591801
30	8	O	1.080806	-2.786405	-0.468099
31	6	C	1.802206	-3.155304	-1.661199
32	6	C	3.255306	-3.290002	-1.199899
33	6	C	3.129807	-3.739402	0.281201
34	1	H	1.409506	-3.106004	1.535401
35	1	H	1.122608	-4.576805	0.574301
36	1	H	1.405407	-4.106204	-2.036799
37	1	H	1.636505	-2.379504	-2.406899
38	1	H	3.811007	-4.001502	-1.812099
39	1	H	3.757405	-2.322902	-1.266099
40	1	H	3.463508	-4.767802	0.426701
41	1	H	3.723606	-3.099502	0.934801
42	6	C	0.399899	3.763195	-0.568699
43	8	O	0.278600	2.937095	0.612101
44	6	C	1.249200	3.426996	1.559501
45	6	C	2.483399	3.728497	0.710001
46	6	C	1.888399	4.164396	-0.654099
47	1	H	0.052300	3.172294	-1.415199
48	1	H	-0.247502	4.638394	-0.451099
49	1	H	0.855499	4.331495	2.039101
50	1	H	1.396500	2.654196	2.313001
51	1	H	3.112698	4.496598	1.161501
52	1	H	3.082000	2.822897	0.595501
53	1	H	1.986998	5.239296	-0.812299
54	1	H	2.387199	3.658197	-1.480999
55	6	C	-4.046097	-0.224410	-0.204099
56	6	C	-5.235697	-0.051911	-0.856299
57	6	C	-6.377597	-0.227912	-0.007199
58	6	C	-6.044096	-0.531212	1.282501
59	16	S	-4.312496	-0.608610	1.474301
60	1	H	-5.301297	0.194089	-1.909199
61	1	H	-7.401697	-0.131413	-0.346999
62	1	H	-6.698696	-0.714012	2.122101
63	35	Br	-2.114397	-0.060908	-0.983599

E(RB3LYP) = –3922.60974866 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.535659
Thermal correction to Energy = 0.552717
Thermal correction to Enthalpy 0.553335
Thermal correction to Gibbs Free Energy = 0.497427
Sum of electronic and zero-point Energies = -3922.074090
Sum of electronic and thermal Energies = -3922.057032
Sum of electronic and thermal Enthalpies = -3922.056414
Sum of electronic and thermal Free Energies = -3922.112321

Table C34. Cartesian coordinates and energies for Transition state **TS–1B (Cl)** found in Figure 5.7 and Figure 5.9. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-6.472411	-0.052863	0.083402
2	1	H	-6.408308	0.548837	0.996302
3	1	H	-7.422013	-0.595959	0.107902
4	1	H	-6.504308	0.638337	-0.765198
5	6	C	-5.276715	-1.005469	-0.030698
6	1	H	-5.279719	-1.705569	0.813802
7	1	H	-5.376518	-1.617068	-0.935698
8	6	C	-3.923112	-0.272075	-0.067998
9	1	H	-3.839209	0.346925	0.836002
10	1	H	-3.931909	0.434225	-0.909198
11	6	C	-2.707816	-1.170281	-0.176298
12	1	H	-2.712319	-1.744681	-1.112498
13	1	H	-2.622319	-1.860381	0.670402
14	3	Li	-0.198617	-1.285992	1.473002
15	6	C	4.791375	-3.023215	-0.227698
16	1	H	4.850378	-2.534616	-1.206398
17	1	H	5.507671	-3.850719	-0.225598
18	1	H	5.120679	-2.295717	0.522102
19	6	C	3.363273	-3.500109	0.061102
20	1	H	3.064270	-4.247407	-0.685298
21	1	H	3.331371	-4.011309	1.031802
22	6	C	2.321878	-2.366904	0.066302
23	1	H	2.397881	-1.845804	-0.902298
24	1	H	2.645782	-1.619905	0.807802
25	6	C	0.857876	-2.778797	0.341902
26	1	H	0.841774	-3.295097	1.321602
27	1	H	0.611173	-3.604996	-0.354898
28	3	Li	-0.398819	-1.749091	-1.041398
29	6	C	1.918297	1.531498	-0.079098
30	6	C	0.594998	1.831204	-0.041498
31	6	C	0.350004	3.235705	0.059202
32	6	C	1.497008	3.983900	0.096402
33	16	S	2.916203	2.985493	0.008102
34	1	H	-0.639694	3.676010	0.101502
35	1	H	1.598713	5.057899	0.168702
36	1	H	2.404992	0.569396	-0.155098
37	17	Cl	-0.964309	0.377611	-0.121198

E(RB3LYP) = –1343.57012777 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.297835		
Thermal correction to Energy =		0.308536		
Thermal correction to Enthalpy		0.309154		
Thermal correction to Gibbs Free Energy =		0.268331		
Sum of electronic and zero-point Energies =		-1343.272293		
Sum of electronic and thermal Energies =		-1343.261591		
Sum of electronic and thermal Enthalpies =		-1343.260973		
Sum of electronic and thermal Free Energies =		-1343.301797		

Table C35. Cartesian coordinates and energies for Transition state **TS–1B (Br)** found in Figure 5.7 and Figure 5.9. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-3.840497	3.016398	1.373905
2	1	H	-4.090598	2.087798	1.898305
3	1	H	-4.754396	3.613799	1.300205
4	1	H	-3.130896	3.568397	1.999605
5	6	C	-3.240197	2.719597	-0.004895
6	1	H	-3.977498	2.188898	-0.620295
7	1	H	-3.025096	3.659797	-0.527595
8	6	C	-1.952998	1.878095	0.061505
9	1	H	-2.187199	0.952696	0.606705
10	1	H	-1.220497	2.411794	0.683105
11	6	C	-1.316299	1.540494	-1.280595
12	1	H	-0.980997	2.440494	-1.805995
13	1	H	-2.063299	1.064095	-1.943495
14	3	Li	-1.041302	-0.656006	-1.674795
15	6	C	-5.653504	-2.263200	0.727105
16	1	H	-5.542703	-1.874000	1.745105
17	1	H	-6.417205	-3.046899	0.751905
18	1	H	-6.034003	-1.446499	0.104105
19	6	C	-4.314804	-2.783502	0.190705
20	1	H	-3.965506	-3.618002	0.812505
21	1	H	-4.454005	-3.194301	-0.817695
22	6	C	-3.213103	-1.711103	0.138805
23	1	H	-3.109702	-1.290103	1.151505
24	1	H	-3.588302	-0.871203	-0.466395
25	6	C	-1.833904	-2.167005	-0.387795
26	1	H	-1.994404	-2.631505	-1.381395
27	1	H	-1.515205	-3.037705	0.220205
28	3	Li	-0.289302	-1.282007	0.768405
29	6	C	3.629000	0.527788	0.932105
30	6	C	2.912399	-0.016711	-0.088095
31	6	C	3.570098	-1.137412	-0.686695
32	6	C	4.778097	-1.422414	-0.109795
33	16	S	5.143799	-0.323614	1.184005
34	1	H	3.161997	-1.704112	-1.514995
35	1	H	5.477796	-2.205215	-0.365995
36	1	H	3.387501	1.373788	1.559505
37	35	Br	0.987700	0.670391	-0.708895

E(RB3LYP) = –3457.50834528 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.296776
Thermal correction to Energy = 0.307706
Thermal correction to Enthalpy 0.308324
Thermal correction to Gibbs Free Energy = 0.266347
Sum of electronic and zero-point Energies = -3457.211569
Sum of electronic and thermal Energies = -3457.200639
Sum of electronic and thermal Enthalpies = -3457.200021
Sum of electronic and thermal Free Energies = -3457.241998

Table C36. Cartesian coordinates and energies for Transition state **TS–3B (Cl)** found in Figure 5.8 and Figure 5.9. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	3.397102	2.623498	-1.611289
2	1	H	2.853602	3.367897	-1.019789
3	1	H	4.142702	3.154098	-2.211089
4	1	H	3.931502	1.974498	-0.909489
5	6	C	2.435602	1.809097	-2.484389
6	1	H	1.918202	2.469997	-3.190089
7	1	H	3.002102	1.095597	-3.095089
8	6	C	1.381202	1.042797	-1.659589
9	1	H	0.833602	1.774897	-1.055189
10	1	H	1.928503	0.432797	-0.927589
11	6	C	0.397203	0.204396	-2.461789
12	1	H	0.866103	-0.636903	-2.985789
13	1	H	-0.135997	0.810996	-3.196889
14	3	Li	0.447503	-1.216604	-0.558589
15	6	C	3.832203	0.145298	3.341811
16	1	H	4.507603	-0.139202	2.527311
17	1	H	4.316103	-0.125702	4.285311
18	1	H	3.734702	1.236098	3.317411
19	6	C	2.464803	-0.529003	3.179911
20	1	H	2.580003	-1.619303	3.240111
21	1	H	1.810003	-0.247803	4.014611
22	6	C	1.764603	-0.178403	1.855611
23	1	H	2.453503	-0.447903	1.042911
24	1	H	1.687402	0.917497	1.793911
25	6	C	0.381403	-0.811104	1.609211
26	1	H	-0.256697	-0.519904	2.470711
27	1	H	0.472504	-1.903404	1.755611
28	3	Li	-1.239197	0.244996	0.774511
29	6	C	-1.567998	3.029896	-0.262789
30	8	O	-1.350398	2.150996	0.870111
31	6	C	-0.682098	2.916196	1.893911
32	6	C	0.298001	3.790196	1.119211
33	6	C	-0.485899	4.130196	-0.169689
34	1	H	-1.497498	2.414696	-1.158889
35	1	H	-2.577499	3.445595	-0.193089
36	1	H	-1.421199	3.516296	2.438911
37	1	H	-0.212398	2.211596	2.580511
38	1	H	0.597301	4.677496	1.678911
39	1	H	1.194802	3.212497	0.886211
40	1	H	-0.950599	5.114896	-0.095989
41	1	H	0.162501	4.131796	-1.046789
42	6	C	2.610104	-3.205603	0.138211
43	8	O	2.061304	-2.326003	-0.872189
44	6	C	3.141704	-2.078103	-1.795589
45	6	C	4.353904	-1.848202	-0.894889
46	6	C	4.087904	-2.790802	0.306711
47	1	H	2.013804	-3.082703	1.039611
48	1	H	2.520905	-4.238203	-0.216089
49	1	H	3.273704	-2.959802	-2.435189

50	1	H	2.870903	-1.226103	-2.414589
51	1	H	5.293104	-2.064902	-1.405789
52	1	H	4.375903	-0.806502	-0.568189
53	1	H	4.737704	-3.667102	0.284911
54	1	H	4.248604	-2.278102	1.255311
55	6	C	-3.706696	-1.987905	0.246611
56	6	C	-3.522397	-0.959305	-0.621189
57	6	C	-4.693897	-0.164706	-0.809389
58	6	C	-5.761897	-0.613106	-0.079889
59	16	S	-5.354796	-2.016006	0.860611
60	1	H	-4.738997	0.700994	-1.458989
61	1	H	-6.763597	-0.209206	-0.035589
62	1	H	-3.004196	-2.738405	0.579711
63	17	Cl	-1.714897	-0.490004	-1.471589

E(RB3LYP) = –1808.67393038 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.534978		
Thermal correction to Energy =		0.552065		
Thermal correction to Enthalpy		0.552683		
Thermal correction to Gibbs Free Energy =		0.497448		
Sum of electronic and zero-point Energies =		-1808.138953		
Sum of electronic and thermal Energies =		-1808.121865		
Sum of electronic and thermal Enthalpies =		-1808.121247		
Sum of electronic and thermal Free Energies =		-1808.176483		

Table C37. Cartesian coordinates and energies for Transition state **TS–3B (Br)** found in Figure 5.8 and Figure 5.9. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	3.807224	2.012375	-1.978908
2	1	H	3.497130	2.853877	-1.350808
3	1	H	4.521727	2.391870	-2.715608
4	1	H	4.335819	1.301271	-1.335508
5	6	C	2.596219	1.350584	-2.646608
6	1	H	2.086424	2.071788	-3.296708
7	1	H	2.931413	0.535782	-3.300008
8	6	C	1.578215	0.795991	-1.629908
9	1	H	1.266421	1.621494	-0.982408
10	1	H	2.133210	0.120987	-0.963708
11	6	C	0.350510	0.118300	-2.237008
12	1	H	0.617603	-0.771701	-2.822208
13	1	H	-0.157085	0.810004	-2.915108
14	3	Li	0.524801	-1.134201	-0.286508
15	6	C	4.387409	0.000271	3.203192
16	1	H	4.949206	-0.452533	2.378692
17	1	H	4.897307	-0.261333	4.135692
18	1	H	4.450817	1.087270	3.081792
19	6	C	2.927206	-0.466718	3.194092
20	1	H	2.884998	-1.552918	3.348792
21	1	H	2.389209	-0.020414	4.040292

22	6	C	2.181408	-0.124113	1.893492
23	1	H	2.752805	-0.565217	1.064292
24	1	H	2.263416	0.960786	1.730992
25	6	C	0.703705	-0.553202	1.808692
26	1	H	0.190608	-0.091698	2.679092
27	1	H	0.644097	-1.629802	2.056392
28	3	Li	-0.844186	0.659309	1.046792
29	6	C	-0.780766	3.345609	-0.289208
30	8	O	-0.591572	2.557507	0.913492
31	6	C	0.271433	3.304801	1.794792
32	6	C	1.293638	3.939194	0.858292
33	6	C	0.455940	4.266300	-0.400108
34	1	H	-0.884871	2.643910	-1.116408
35	1	H	-1.706662	3.919616	-0.189008
36	1	H	-0.319761	4.060405	2.326792
37	1	H	0.694228	2.604898	2.515892
38	1	H	1.766145	4.821090	1.293192
39	1	H	2.072933	3.210988	0.625692
40	1	H	0.150548	5.314002	-0.405508
41	1	H	1.016539	4.077396	-1.316508
42	6	C	2.456984	-3.357215	0.397192
43	8	O	1.877791	-2.534611	-0.643608
44	6	C	2.834990	-2.541218	-1.723308
45	6	C	4.182392	-2.376728	-1.022108
46	6	C	3.983586	-3.140826	0.311392
47	1	H	2.020687	-3.043912	1.343092
48	1	H	2.187677	-4.401013	0.203792
49	1	H	2.768283	-3.498917	-2.254608
50	1	H	2.579496	-1.735516	-2.408008
51	1	H	5.008089	-2.768034	-1.618208
52	1	H	4.369999	-1.317429	-0.833608
53	1	H	4.507479	-4.098030	0.309392
54	1	H	4.349690	-2.560929	1.159092
55	6	C	-4.927592	-0.127961	-0.485008
56	6	C	-3.759796	-0.752969	-0.176508
57	6	C	-3.899803	-1.684768	0.900192
58	6	C	-5.176004	-1.752359	1.389592
59	16	S	-6.242996	-0.674951	0.542992
60	1	H	-3.083008	-2.280274	1.290292
61	1	H	-5.557708	-2.369756	2.190292
62	1	H	-5.124186	0.617041	-1.242508
63	35	Br	-1.877594	-0.374183	-1.108808

E(RB3LYP) = –3922.60953464 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.534914	
Thermal correction to Energy =	0.552220	
Thermal correction to Enthalpy	0.552838	
Thermal correction to Gibbs Free Energy =	0.496134	
Sum of electronic and zero-point Energies =	-3922.074620	
Sum of electronic and thermal Energies =	-3922.057315	
Sum of electronic and thermal Enthalpies =	-3922.056697	
Sum of electronic and thermal Free Energies =	-3922.113401	

Table C38. Cartesian coordinates and energies for Transition state **TS–2A (Cl)** found in Figure 5.10 and Figure 5.11. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	-0.879388	-0.319912	1.595806
2	6	C	-3.495912	3.737873	-1.151394
3	1	H	-2.725514	4.194777	-1.781894
4	1	H	-4.318216	4.453868	-1.058394
5	1	H	-3.877807	2.858671	-1.681294
6	6	C	-2.924409	3.346076	0.216006
7	1	H	-2.577815	4.241978	0.745606
8	1	H	-3.717407	2.910472	0.836206
9	6	C	-1.759904	2.342483	0.120906
10	1	H	-0.971506	2.789987	-0.501394
11	1	H	-2.119699	1.466281	-0.439294
12	6	C	-1.159301	1.900986	1.446406
13	1	H	-1.924898	1.433882	2.091806
14	1	H	-0.740006	2.739989	2.008406
15	3	Li	0.075812	-0.366107	-1.024994
16	6	C	-1.369281	-1.632615	-0.078594
17	6	C	-1.166873	-2.972014	0.226406
18	6	C	-2.295768	-3.846020	0.094606
19	6	C	-3.419972	-3.188827	-0.323094
20	16	S	-3.068281	-1.499425	-0.545294
21	1	H	-0.197771	-3.345608	0.547806
22	1	H	-2.270462	-4.909820	0.302306
23	1	H	-4.405069	-3.595632	-0.503694
24	6	C	2.816909	0.203709	0.330106
25	6	C	3.337216	-1.000988	0.712506
26	6	C	4.569617	-1.318881	0.051006
27	6	C	4.965412	-0.356878	-0.834694
28	16	S	3.825904	0.965015	-0.865794
29	1	H	2.862019	-1.646191	1.441906
30	1	H	5.134123	-2.225777	0.230806
31	1	H	5.848512	-0.337073	-1.456894
32	17	Cl	1.041404	0.958199	0.895406

E(RB3LYP) = –1738.17752886 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction =	0.233647
Thermal correction to Energy =	0.243782
Thermal correction to Enthalpy	0.244400
Thermal correction to Gibbs Free Energy =	0.203793
Sum of electronic and zero-point Energies =	-1737.943882
Sum of electronic and thermal Energies =	-1737.933747
Sum of electronic and thermal Enthalpies =	-1737.933129
Sum of electronic and thermal Free Energies =	-1737.973736

Table C39. Cartesian coordinates and energies for Transition state **TS–2A (Br)** found in Figure 5.10 and Figure 5.11. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	0.836063	6.024199	-0.196904
2	1	H	0.343163	6.057497	-1.174204
3	1	H	1.547859	6.853902	-0.153704
4	1	H	0.069562	6.201196	0.564796
5	6	C	1.526069	4.673602	0.023696
6	1	H	2.308969	4.530406	-0.731604
7	1	H	2.035469	4.673304	0.995396
8	6	C	0.553474	3.483298	-0.031204
9	1	H	0.039374	3.496696	-1.001804
10	1	H	-0.232927	3.638995	0.718896
11	6	C	1.195180	2.118401	0.182196
12	1	H	1.685180	2.093103	1.168196
13	1	H	1.990480	1.956304	-0.560804
14	3	Li	1.308489	0.029301	-1.307504
15	3	Li	1.373289	0.015102	1.362396
16	6	C	2.529694	-1.196993	-0.005204
17	6	C	3.913693	-1.100188	-0.044104
18	16	S	2.168701	-2.926695	-0.004104
19	6	C	4.648699	-2.330784	-0.071304
20	1	H	4.419389	-0.137985	-0.052904
21	6	C	3.833504	-3.428988	-0.053704
22	1	H	5.730599	-2.393680	-0.102104
23	1	H	4.115408	-4.472487	-0.066904
24	6	C	-2.430008	-0.725115	0.006296
25	6	C	-2.323702	-2.090714	-0.011204
26	6	C	-3.586699	-2.768520	-0.058004
27	6	C	-4.651603	-1.912224	-0.075504
28	16	S	-4.107210	-0.254422	-0.034604
29	1	H	-1.369700	-2.605910	0.009596
30	1	H	-3.693295	-3.846620	-0.077204
31	1	H	-5.705402	-2.148629	-0.109204
32	35	Br	-0.759414	0.639792	0.086796

E(RB3LYP) = –3852.11274592 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.234004	
Thermal correction to Energy =	0.244336	
Thermal correction to Enthalpy	0.244954	
Thermal correction to Gibbs Free Energy =	0.203708	
Sum of electronic and zero-point Energies =	-3851.878742	
Sum of electronic and thermal Energies =	-3851.868410	
Sum of electronic and thermal Enthalpies =	-3851.867792	
Sum of electronic and thermal Free Energies =	-3851.909038	

Table C40. Cartesian coordinates and energies for Transition state **TS–4A (Cl)** found in Figure 5.12 and Figure 5.13. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-1.239906	0.508196	0.767202
2	6	C	3.846297	2.378988	-1.122198
3	1	H	3.441598	2.999288	-0.315798
4	1	H	4.611398	2.963487	-1.641998
5	1	H	4.340096	1.520087	-0.655898
6	6	C	2.733496	1.921990	-2.072298
7	1	H	2.266498	2.792790	-2.548598
8	1	H	3.158995	1.321189	-2.885098
9	6	C	1.640795	1.097991	-1.362198
10	1	H	1.237796	1.705492	-0.544098
11	1	H	2.149894	0.261591	-0.863298
12	6	C	0.503694	0.610393	-2.254898
13	1	H	0.853693	-0.064307	-3.045998
14	1	H	0.003396	1.452294	-2.740198
15	3	Li	0.421191	-1.089807	-0.735498
16	6	C	2.739889	-2.853210	-0.036798
17	8	O	1.901289	-2.340809	-1.098598
18	6	C	2.756889	-2.284610	-2.261498
19	6	C	4.134690	-1.832813	-1.739098
20	6	C	4.067190	-2.111313	-0.212898
21	1	H	2.236689	-2.664410	0.908202
22	1	H	2.859287	-3.934711	-0.178398
23	1	H	2.805388	-3.285310	-2.705498
24	1	H	2.305491	-1.599510	-2.976398
25	1	H	4.936389	-2.389714	-2.226498
26	1	H	4.297592	-0.772313	-1.935498
27	1	H	4.911689	-2.700814	0.147202
28	1	H	4.039691	-1.176613	0.349202
29	6	C	-1.091001	3.319296	-0.196898
30	8	O	-1.107103	2.409496	0.932502
31	6	C	-0.496502	3.096595	2.045002
32	6	C	0.665600	3.857093	1.415002
33	6	C	0.113700	4.261094	0.026802
34	1	H	-1.014200	2.709196	-1.095300
35	1	H	-2.037200	3.868698	-0.214500
36	1	H	-1.231700	3.773196	2.497702
37	1	H	-0.195100	2.344494	2.773702
38	1	H	0.972901	4.715493	2.014202
39	1	H	1.521899	3.187792	1.311602
40	1	H	-0.211400	5.302794	0.019102
41	1	H	0.866100	4.140593	-0.753400
42	6	C	0.286292	-0.801310	1.464602
43	6	C	-0.005610	-1.916010	2.238302
44	6	C	0.864990	-2.185310	3.345902
45	6	C	1.867091	-1.260410	3.459502
46	16	S	1.717893	-0.072710	2.196602
47	1	H	-0.848710	-2.563700	2.011102
48	1	H	0.751888	-3.026810	4.020402
49	1	H	2.658491	-1.218110	4.194702

50	6	C	-3.464410	-0.895500	-0.823100
51	6	C	-3.639410	-2.041300	-0.098800
52	6	C	-4.990210	-2.224400	0.345602
53	6	C	-5.821910	-1.210300	-0.037800
54	16	S	-4.953410	-0.008200	-0.958800
55	1	H	-5.324110	-3.077000	0.924502
56	1	H	-6.879210	-1.098190	0.154102
57	1	H	-2.834010	-2.733900	0.114502
58	17	Cl	-1.708810	-0.225000	-1.495200

E(RB3LYP) = –2203.28198001 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.471300		
Thermal correction to Energy =		0.487837		
Thermal correction to Enthalpy		0.488455		
Thermal correction to Gibbs Free Energy =		0.433231		
Sum of electronic and zero-point Energies =		-2202.810680		
Sum of electronic and thermal Energies =		-2202.794143		
Sum of electronic and thermal Enthalpies =		-2202.793525		
Sum of electronic and thermal Free Energies =		-2202.848749		

Table C41. Cartesian coordinates and energies for Transition state **TS–4A (Br)** found in Figure 5.12 and Figure 5.13. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-4.479280	1.316653	-1.623604
2	1	H	-4.776863	0.384480	-1.131812
3	1	H	-5.274048	1.593945	-2.322773
4	1	H	-4.430355	2.090800	-0.851036
5	6	C	-3.127453	1.158868	-2.329429
6	1	H	-3.212678	0.418655	-3.134807
7	1	H	-2.846958	2.102719	-2.812931
8	6	C	-1.993419	0.733014	-1.378087
9	1	H	-2.316695	-0.201004	-0.894653
10	1	H	-1.945509	1.459752	-0.559992
11	6	C	-0.608638	0.590078	-2.025076
12	1	H	-0.294853	1.558405	-2.429030
13	1	H	-0.652056	-0.095912	-2.884173
14	3	Li	0.559705	1.127673	0.810848
15	3	Li	-0.285868	-1.041734	-0.578543
16	6	C	-2.147274	-2.733120	-2.237070
17	8	O	-1.338359	-2.620036	-1.043878
18	6	C	-2.027340	-3.380519	-0.025583
19	6	C	-3.496135	-3.009263	-0.221433
20	6	C	-3.612526	-2.794412	-1.752843
21	1	H	-1.926113	-1.873278	-2.866850
22	1	H	-1.860083	-3.647992	-2.766280
23	1	H	-1.850889	-4.449012	-0.202389
24	1	H	-1.613349	-3.098432	0.940073

25	1	H	-4.169863	-3.782366	0.151225
26	1	H	-3.706370	-2.082687	0.315660
27	1	H	-4.143090	-3.615018	-2.238466
28	1	H	-4.144478	-1.870620	-1.983568
29	6	C	-1.207607	3.217683	2.086926
30	8	O	-0.311549	2.840395	1.020510
31	6	C	-0.498570	3.808166	-0.040095
32	6	C	-1.976947	4.248218	0.041700
33	6	C	-2.490140	3.625820	1.364945
34	1	H	-1.317550	2.358503	2.747177
35	1	H	-0.768950	4.055205	2.643406
36	1	H	0.182466	4.648354	0.129863
37	1	H	-0.235310	3.316478	-0.975520
38	1	H	-2.051250	5.336625	0.054943
39	1	H	-2.546850	3.884789	-0.814070
40	1	H	-3.090170	4.320757	1.953986
41	1	H	-3.094180	2.738758	1.164971
42	6	C	-0.284640	-0.662020	1.594631
43	6	C	0.391579	-1.658520	2.283710
44	6	C	-0.316520	-2.305830	3.350059
45	6	C	-1.581360	-1.810620	3.515744
46	16	S	-1.877390	-0.553670	2.348197
47	1	H	1.408885	-1.940730	2.023998
48	1	H	0.095561	-3.101160	3.961153
49	1	H	-2.327920	-2.108600	4.238545
50	6	C	3.887771	-0.027600	-0.698870
51	6	C	5.003609	0.023798	-1.485720
52	6	C	6.209822	-0.246290	-0.760460
53	6	C	5.993629	-0.500880	0.563980
54	16	S	4.296251	-0.416070	0.949396
55	1	H	4.971531	0.244841	-2.545060
56	1	H	7.194530	-0.250270	-1.211290
57	1	H	6.716442	-0.732390	1.332381
58	35	Br	1.939188	0.236350	-1.246990

E(RB3LYP) = –4317.21672185 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.471397	
Thermal correction to Energy =	0.487977	
Thermal correction to Enthalpy	0.488595	
Thermal correction to Gibbs Free Energy =	0.432977	
Sum of electronic and zero-point Energies =	-4316.745325	
Sum of electronic and thermal Energies =	-4316.728745	
Sum of electronic and thermal Enthalpies =	-4316.728127	
Sum of electronic and thermal Free Energies =	-4316.783744	

Table C42. Cartesian coordinates and energies for Transition state **TS–2B (Cl)** found in Figure 5.14 and Figure 5.16. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	0.203799	0.370203	-0.878495
2	6	C	-3.789693	-3.761204	-1.263495
3	1	H	-4.107195	-2.842104	-1.767595
4	1	H	-4.663892	-4.413505	-1.177895
5	1	H	-3.063193	-4.260103	-1.913695
6	6	C	-3.176394	-3.451203	0.106605
7	1	H	-3.928295	-2.978604	0.750305
8	1	H	-2.889692	-4.385002	0.605105
9	6	C	-1.941796	-2.534201	0.022405
10	1	H	-2.240897	-1.609601	-0.492795
11	1	H	-1.200395	-3.010899	-0.633495
12	6	C	-1.286396	-2.201099	1.349805
13	1	H	-0.904295	-3.083099	1.867605
14	1	H	-1.980797	-1.690201	2.037705
15	3	Li	-0.941300	0.087201	1.578205
16	6	C	-2.558903	1.548498	-0.358895
17	6	C	-1.250903	1.626001	0.058905
18	6	C	-0.952305	3.017601	0.346105
19	6	C	-1.976707	3.905399	0.148905
20	16	S	-3.407005	3.097697	-0.408995
21	1	H	0.017994	3.357903	0.696805
22	1	H	-1.981309	4.976899	0.294905
23	1	H	-3.128601	0.676197	-0.657595
24	6	C	3.230399	0.634008	0.527105
25	6	C	2.721601	-0.576492	0.176805
26	6	C	3.574202	-1.304691	-0.708695
27	6	C	4.726701	-0.631289	-1.014495
28	16	S	4.795798	0.915611	-0.227495
29	1	H	3.343604	-2.289091	-1.098295
30	1	H	5.541302	-0.946687	-1.651195
31	1	H	2.817098	1.391508	1.178105
32	17	Cl	0.849502	-1.300396	0.805905

E(RB3LYP) = –1738.16419785 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.233291		
Thermal correction to Energy =		0.243428		
Thermal correction to Enthalpy		0.244046		
Thermal correction to Gibbs Free Energy =		0.203866		
Sum of electronic and zero-point Energies =		-1737.930906		
Sum of electronic and thermal Energies =		-1737.920770		
Sum of electronic and thermal Enthalpies =		-1737.920152		
Sum of electronic and thermal Free Energies =		-1737.960332		

Table C43. Cartesian coordinates and energies for Transition state **TS–2B (Br)** found in Figure 5.14 and Figure 5.16. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	-0.305006	0.945493	-1.899400
2	6	C	6.432782	-0.162881	0.933500
3	1	H	6.199484	0.036821	1.984800
4	1	H	7.438886	0.219508	0.736500
5	1	H	6.457170	-1.249981	0.802900
6	6	C	5.390289	0.476130	0.009000
7	1	H	5.402801	1.566030	0.135000
8	1	H	5.658387	0.286327	-1.037700
9	6	C	3.962483	-0.042254	0.257800
10	1	H	3.708385	0.140349	1.312300
11	1	H	3.966671	-1.134854	0.146100
12	6	C	2.886390	0.545658	-0.643400
13	1	H	3.073587	0.328356	-1.699400
14	1	H	2.856802	1.646258	-0.551200
15	3	Li	1.025302	1.628978	0.386200
16	6	C	-1.893596	1.853510	0.234100
17	6	C	-0.816690	2.410198	-0.418600
18	6	C	-1.085374	3.822501	-0.613100
19	6	C	-2.284369	4.276514	-0.131200
20	16	S	-3.191583	2.992724	0.604200
21	1	H	-0.392567	4.497694	-1.107100
22	1	H	-2.689858	5.278619	-0.161600
23	1	H	-2.045407	0.825112	0.542300
24	6	C	-1.531047	-2.779694	-0.912100
25	6	C	-0.927738	-2.005300	0.029500
26	6	C	-1.693737	-1.922092	1.236100
27	6	C	-2.860245	-2.636779	1.190500
28	16	S	-3.060154	-3.436377	-0.337800
29	1	H	-1.388431	-1.351095	2.105200
30	1	H	-3.613846	-2.744971	1.957900
31	1	H	-1.200149	-3.025997	-1.911400
32	35	Br	0.884575	-0.827320	-0.286000

E(RB3LYP) = –3852.09948841 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.232806
Thermal correction to Energy = 0.243277
Thermal correction to Enthalpy 0.243895
Thermal correction to Gibbs Free Energy = 0.202082
Sum of electronic and zero-point Energies = -3851.866682
Sum of electronic and thermal Energies = -3851.856211
Sum of electronic and thermal Enthalpies = -3851.855593
Sum of electronic and thermal Free Energies = -3851.897406

Table C44. Cartesian coordinates and energies for Transition state **TS–4B (Cl)** found in Figure 5.15 and Figure 5.16. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-0.450751	-0.836397	-0.923908
2	6	C	-4.067103	2.360113	-0.452759
3	1	H	-4.433374	1.387240	-0.108312
4	1	H	-4.932242	2.946500	-0.776225
5	1	H	-3.624945	2.867977	0.410229
6	6	C	-3.040989	2.193075	-1.579104
7	1	H	-3.515470	1.722125	-2.448332
8	1	H	-2.692616	3.176346	-1.917356
9	6	C	-1.818694	1.349701	-1.162562
10	1	H	-2.210393	0.393134	-0.788249
11	1	H	-1.355380	1.824483	-0.290413
12	6	C	-0.774705	1.141938	-2.250591
13	1	H	-0.386577	2.095494	-2.615324
14	1	H	-1.150807	0.572814	-3.107319
15	3	Li	1.288576	0.542276	0.664539
16	6	C	0.439641	2.822000	2.371362
17	8	O	1.013779	2.391893	1.120074
18	6	C	0.906554	3.500123	0.194306
19	6	C	-0.331830	4.311750	0.638030
20	6	C	-0.780966	3.640232	1.959042
21	1	H	0.205911	1.929159	2.951531
22	1	H	1.173012	3.430387	2.914866
23	1	H	1.822420	4.096471	0.255960
24	1	H	0.822927	3.073861	-0.803919
25	1	H	-0.065139	5.357903	0.796069
26	1	H	-1.120929	4.278676	-0.113876
27	1	H	-1.070971	4.362564	2.723307
28	1	H	-1.626261	2.972039	1.784594
29	6	C	-2.840612	-1.878948	-2.481106
30	8	O	-1.884230	-2.087407	-1.417705
31	6	C	-2.596364	-2.841523	-0.409019
32	6	C	-3.967672	-2.167260	-0.337849
33	6	C	-4.193750	-1.640900	-1.780940
34	1	H	-2.495730	-1.038380	-3.079770
35	1	H	-2.865430	-2.778170	-3.106580
36	1	H	-2.673180	-3.884060	-0.741620
37	1	H	-2.022710	-2.793080	0.512817
38	1	H	-4.745430	-2.859790	-0.012770
39	1	H	-3.929150	-1.340730	0.373922
40	1	H	-4.994470	-2.175670	-2.294100
41	1	H	-4.450670	-0.580870	-1.775810
42	6	C	0.324519	-2.053520	1.756781
43	6	C	-0.178820	-0.877270	1.257492
44	6	C	-1.357410	-0.527200	2.027582
45	6	C	-1.704550	-1.397610	3.026339
46	16	S	-0.596150	-2.731250	3.110619
47	1	H	-1.951750	0.359835	1.830280
48	1	H	-2.538620	-1.343210	3.712710
49	1	H	1.190984	-2.617390	1.431132

50	6	C	4.391421	0.387492	-0.922550
51	6	C	3.317338	-0.392650	-1.208560
52	6	C	3.547074	-1.779870	-0.957740
53	6	C	4.808457	-2.034160	-0.490560
54	16	S	5.743491	-0.577850	-0.340620
55	1	H	2.805403	-2.553450	-1.116480
56	1	H	5.248819	-2.985000	-0.225230
57	1	H	4.504092	1.458976	-1.005780
58	17	Cl	1.451890	0.314280	-1.748020

E(RB3LYP) = –2203.26827781 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.470828
Thermal correction to Energy = 0.487484
Thermal correction to Enthalpy 0.488102
Thermal correction to Gibbs Free Energy = 0.432582
Sum of electronic and zero-point Energies = -2202.787449
Sum of electronic and thermal Energies = -2202.780794
Sum of electronic and thermal Enthalpies = -2202.780176
Sum of electronic and thermal Free Energies = -2202.835696

Table C45. Cartesian coordinates and energies for Transition state **TS–4B (Br)** found in Figure 5.15 and Figure 5.16. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-0.918302	0.612693	1.045203
2	6	C	4.081591	2.162814	-1.306897
3	1	H	3.819888	2.806813	-0.461197
4	1	H	4.864489	2.668918	-1.879497
5	1	H	4.510495	1.242216	-0.897097
6	6	C	2.851792	1.859509	-2.170097
7	1	H	2.438088	2.791907	-2.572897
8	1	H	3.145695	1.256910	-3.037997
9	6	C	1.743796	1.114604	-1.400897
10	1	H	1.460393	1.721703	-0.533997
11	1	H	2.210899	0.215706	-0.974097
12	6	C	0.500897	0.775399	-2.222697
13	1	H	0.735400	0.125000	-3.074297
14	1	H	0.061493	1.691197	-2.627797
15	3	Li	0.507605	-0.992201	-0.669997
16	6	C	2.724713	-2.936491	-0.311997
17	8	O	1.827510	-2.315195	-1.261597
18	6	C	2.576810	-2.232192	-2.495397
19	6	C	4.030709	-1.923686	-2.080197
20	6	C	4.064810	-2.244986	-0.562197
21	1	H	2.316513	-2.784493	0.683803
22	1	H	2.775318	-4.010591	-0.529497
23	1	H	2.502514	-3.195292	-3.011797

24	1	H	2.118407	-1.461494	-3.111797
25	1	H	4.732111	-2.539383	-2.645397
26	1	H	4.279604	-0.878385	-2.266797
27	1	H	4.909413	-2.875082	-0.279997
28	1	H	4.113006	-1.327085	0.026603
29	6	C	-0.604715	3.496694	0.215003
30	8	O	-0.523810	2.479394	1.242203
31	6	C	0.285287	3.013298	2.311103
32	6	C	1.397384	3.772703	1.592603
33	6	C	0.696982	4.322500	0.325703
34	1	H	-0.721413	2.980294	-0.736697
35	1	H	-1.490317	4.112290	0.401503
36	1	H	-0.328716	3.678995	2.929903
37	1	H	0.632491	2.171999	2.910603
38	1	H	1.826981	4.559805	2.213603
39	1	H	2.196487	3.080406	1.321503
40	1	H	0.467377	5.384199	0.428203
41	1	H	1.322382	4.200502	-0.559297
42	6	C	1.822402	-0.311495	1.928203
43	6	C	0.603904	-0.799201	1.524703
44	6	C	0.297909	-1.967202	2.330403
45	6	C	1.237711	-2.319298	3.263703
46	16	S	2.588306	-1.229092	3.230003
47	1	H	-0.612288	-2.548906	2.212203
48	1	H	1.223514	-3.143998	3.963103
49	1	H	2.374898	0.537807	1.547003
50	6	C	-4.827500	0.150876	-0.766797
51	6	C	-3.671497	-0.542419	-0.586197
52	6	C	-3.839092	-1.681420	0.263603
53	6	C	-5.123392	-1.834826	0.710903
54	16	S	-6.165297	-0.585830	0.102303
55	1	H	-3.035089	-2.357917	0.528603
56	1	H	-5.524288	-2.604027	1.355603
57	1	H	-5.004404	1.045475	-1.346397
58	35	Br	-1.754000	0.030489	-1.361097

E(RB3LYP) = –4317.20406773 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.470756	
Thermal correction to Energy =	0.487513	
Thermal correction to Enthalpy	0.488131	
Thermal correction to Gibbs Free Energy =	0.432336	
Sum of electronic and zero-point Energies =	-4316.733311	
Sum of electronic and thermal Energies =	-4316.716555	
Sum of electronic and thermal Enthalpies =	-4316.715937	
Sum of electronic and thermal Free Energies =	-4316.771732	

Table C46. Cartesian coordinates and energies for Transition state **TS–2D (Cl)** found in Figure C5 and Figure 5.20. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-0.103603	-0.502313	-1.041702
2	6	C	2.816138	4.314723	-1.173902
3	1	H	3.213147	3.554028	-1.854802
4	1	H	3.572428	5.099232	-1.073602
5	1	H	1.936632	4.758812	-1.652202
6	6	C	2.449545	3.699418	0.181398
7	1	H	3.348550	3.287629	0.656598
8	1	H	2.078236	4.481014	0.855498
9	6	C	1.386859	2.589305	0.078498
10	1	H	1.768368	1.819010	-0.608602
11	1	H	0.499254	3.009794	-0.415402
12	6	C	0.972267	1.951100	1.394898
13	1	H	0.531658	2.682095	2.079898
14	1	H	1.848572	1.515111	1.907798
15	3	Li	0.812294	-0.292202	1.550998
16	6	C	2.817604	-1.056577	-0.239302
17	6	C	1.529610	-1.518293	-0.094002
18	6	C	1.576627	-2.968393	-0.036402
19	6	C	2.819834	-3.534777	-0.137502
20	16	S	4.048619	-2.322062	-0.307402
21	1	H	0.692035	-3.588503	0.080098
22	1	H	3.089947	-4.581774	-0.121002
23	1	H	3.170291	-0.034973	-0.317802
24	6	C	-2.863009	-0.043347	0.320698
25	6	C	-3.252793	-1.301452	0.685898
26	6	C	-4.484388	-1.708867	0.074498
27	6	C	-5.010400	-0.758474	-0.754102
28	16	S	-3.997117	0.662239	-0.793802
29	1	H	-2.685085	-1.921945	1.369098
30	1	H	-4.955476	-2.668573	0.248998
31	1	H	-5.923099	-0.798885	-1.330802
32	17	Cl	-1.157820	0.843674	0.850798

E(RB3LYP) = –1738.16569506 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.233310	
Thermal correction to Energy =	0.243470	
Thermal correction to Enthalpy	0.244088	
Thermal correction to Gibbs Free Energy =	0.203610	
Sum of electronic and zero-point Energies =	-1737.932385	
Sum of electronic and thermal Energies =	-1737.922225	
Sum of electronic and thermal Enthalpies =	-1737.921607	
Sum of electronic and thermal Free Energies =	-1737.962085	

Table C47. Cartesian coordinates and energies for Transition state **TS–2D (Br)** found in Figure C5 and Figure 5.20. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	0.102999	-1.457606	1.361689
2	6	C	6.160300	-1.193517	-0.181411
3	1	H	6.228601	-0.709617	-1.161411
4	1	H	6.949798	-1.948918	-0.126511
5	1	H	6.372301	-0.432817	0.577189
6	6	C	4.772399	-1.808014	0.031089
7	1	H	4.595097	-2.587914	-0.720011
8	1	H	4.735898	-2.309414	1.006289
9	6	C	3.636100	-0.774312	-0.041911
10	1	H	3.685801	-0.267712	-1.015311
11	1	H	3.825302	0.007487	0.705289
12	6	C	2.236599	-1.341610	0.160889
13	1	H	2.177399	-1.822810	1.149589
14	1	H	2.044898	-2.132409	-0.580811
15	3	Li	0.152199	-1.366406	-1.289511
16	6	C	-2.471401	-1.581401	-0.012111
17	6	C	-1.303102	-2.307803	-0.028311
18	6	C	-1.648305	-3.717103	-0.052911
19	6	C	-2.987006	-4.007500	-0.055211
20	16	S	-3.942703	-2.559198	-0.027211
21	1	H	-0.906706	-4.510804	-0.068611
22	1	H	-3.469707	-4.975099	-0.071511
23	1	H	-2.605299	-0.506001	0.007889
24	6	C	-0.266593	2.524795	0.009289
25	6	C	0.216409	3.804994	-0.039911
26	6	C	-0.808089	4.808796	-0.080011
27	6	C	-2.070390	4.286198	-0.060911
28	16	S	-2.009893	2.543198	0.006789
29	1	H	1.275909	4.033792	-0.048011
30	1	H	-0.609187	5.873196	-0.121011
31	1	H	-3.016289	4.807700	-0.082311
32	35	Br	0.868303	0.687093	0.079089

E(RB3LYP) = –3852.10132296 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.233542
Thermal correction to Energy = 0.243929
Thermal correction to Enthalpy 0.244547
Thermal correction to Gibbs Free Energy = 0.203147
Sum of electronic and zero-point Energies = -3851.867781
Sum of electronic and thermal Energies = -3851.857394
Sum of electronic and thermal Enthalpies = -3851.856776
Sum of electronic and thermal Free Energies = -3851.898176

Table C48. Cartesian coordinates and energies for Transition state **TS–4D (Cl)** found in Figure C5 and Figure 5.21. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-0.425369	-0.744810	-0.925730
2	6	C	-3.906522	2.625411	-0.471062
3	1	H	-4.348256	1.677430	-0.145399
4	1	H	-4.717062	3.263785	-0.835142
5	1	H	-3.473466	3.105694	0.413015
6	6	C	-2.837252	2.390412	-1.543868
7	1	H	-3.293808	1.943475	-2.435426
8	1	H	-2.413514	3.349308	-1.866195
9	6	C	-1.693558	1.479641	-1.055910
10	1	H	-2.158894	0.539994	-0.723577
11	1	H	-1.273477	1.921239	-0.145528
12	6	C	-0.574038	1.230257	-2.062167
13	1	H	-0.107918	2.172177	-2.361312
14	1	H	-0.926386	0.729944	-2.972580
15	3	Li	1.149911	0.528678	0.921368
16	6	C	-0.081591	2.864052	2.303990
17	8	O	0.858110	2.394278	1.296544
18	6	C	1.180604	3.470624	0.373424
19	6	C	0.082762	4.509372	0.574077
20	6	C	-0.220164	4.369538	2.074233
21	1	H	-1.028192	2.337903	2.153835
22	1	H	0.313399	2.607270	3.288530
23	1	H	2.166217	3.869643	0.635547
24	1	H	1.215768	3.046066	-0.629125
25	1	H	0.408635	5.512311	0.294786
26	1	H	-0.796025	4.252895	-0.022906
27	1	H	0.521406	4.916354	2.662803
28	1	H	-1.211091	4.734206	2.348256
29	6	C	-2.844903	-1.560493	-2.581530
30	8	O	-1.866195	-1.916409	-1.581260
31	6	C	-2.538362	-2.855344	-0.710763
32	6	C	-3.938224	-2.263517	-0.520204
33	6	C	-4.183816	-1.461631	-1.827622
34	1	H	-2.526467	-0.629335	-3.045478
35	1	H	-2.869572	-2.349601	-3.341775
36	1	H	-2.574744	-3.830707	-1.211708
37	1	H	-1.958194	-2.936722	0.204693
38	1	H	-4.685792	-3.040839	-0.354584
39	1	H	-3.938035	-1.600943	0.346244
40	1	H	-4.998378	-1.876539	-2.423267
41	1	H	-4.427727	-0.421330	-1.606855
42	6	C	0.214240	-2.170268	1.690471
43	6	C	-0.311830	-0.977811	1.256488
44	6	C	-1.561883	-0.754053	1.957739
45	6	C	-1.936266	-1.725805	2.846795
46	16	S	-0.768304	-3.009362	2.902954
47	1	H	-2.187045	0.117816	1.789753
48	1	H	-2.821752	-1.772523	3.466042
49	1	H	1.131778	-2.661027	1.387662

50	6	C	3.490996	-0.360663	-1.092289
51	6	C	4.670690	0.314553	-1.228577
52	6	C	5.797740	-0.414294	-0.721351
53	6	C	5.459142	-1.629677	-0.196690
54	16	S	3.739578	-1.901806	-0.324376
55	1	H	6.815933	-0.044802	-0.748162
56	1	H	6.103610	-2.376089	0.244478
57	1	H	4.741001	1.299710	-1.673805
58	17	Cl	1.650714	0.297973	-1.532374

E(RB3LYP) = –2203.27006684 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.471076	
Thermal correction to Energy =	0.487584	
Thermal correction to Enthalpy	0.488202	
Thermal correction to Gibbs Free Energy =	0.433496	
Sum of electronic and zero-point Energies =	-2202.798991	
Sum of electronic and thermal Energies =	-2202.782483	
Sum of electronic and thermal Enthalpies =	-2202.781865	
Sum of electronic and thermal Free Energies =	-2202.836571	

Table C49. Cartesian coordinates and energies for Transition state **TS–4D (Br)** found in Figure C5 and Figure 5.21. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	-0.535077	1.149571	0.799800
2	6	C	4.378431	1.342340	-1.796638
3	1	H	4.364767	2.061742	-0.971298
4	1	H	5.151780	1.660735	-2.502135
5	1	H	4.683239	0.375646	-1.381675
6	6	C	3.001621	1.244869	-2.464158
7	1	H	2.717846	2.220124	-2.878187
8	1	H	3.048476	0.554299	-3.315242
9	6	C	1.895212	0.774621	-1.501414
10	1	H	1.881569	1.455826	-0.643017
11	1	H	2.225576	-0.187822	-1.083370
12	6	C	0.489611	0.676010	-2.108689
13	1	H	0.495885	0.029385	-2.997788
14	1	H	0.172146	1.666179	-2.452693
15	3	Li	0.229255	-0.965024	-0.624143
16	6	C	1.892229	-3.363735	-0.182660
17	8	O	1.146202	-2.604562	-1.161327
18	6	C	1.890660	-2.716832	-2.396044
19	6	C	3.380141	-2.761262	-1.989791
20	6	C	3.346750	-2.984509	-0.455205
21	1	H	1.529994	-3.083686	0.804057
22	1	H	1.711419	-4.432482	-0.352617
23	1	H	1.584852	-3.637575	-2.904042

24	1	H	1.626981	-1.863068	-3.017970
25	1	H	3.895198	-3.572355	-2.507033
26	1	H	3.887111	-1.829476	-2.243582
27	1	H	4.043244	-3.755462	-0.122523
28	1	H	3.581131	-2.059663	0.075175
29	6	C	0.559612	3.845008	0.046801
30	8	O	0.345633	2.844943	1.071349
31	6	C	1.286335	3.117757	2.131032
32	6	C	2.568552	3.505879	1.398148
33	6	C	2.054137	4.227965	0.127917
34	1	H	0.271008	3.397961	-0.903875
35	1	H	-0.089111	4.702211	0.253009
36	1	H	0.904328	3.940885	2.747332
37	1	H	1.369571	2.215174	2.735348
38	1	H	3.217372	4.135304	2.008690
39	1	H	3.124084	2.605209	1.129928
40	1	H	2.166779	5.309968	0.210670
41	1	H	2.596173	3.902775	-0.760698
42	6	C	1.749121	-0.486894	1.898268
43	6	C	0.433074	-0.601028	1.523315
44	6	C	-0.202943	-1.565664	2.401650
45	6	C	0.598990	-2.128585	3.359961
46	16	S	2.218000	-1.508175	3.262115
47	1	H	-1.249653	-1.844999	2.317308
48	1	H	0.344028	-2.861904	4.112783
49	1	H	2.529102	0.124228	1.461636
50	6	C	-3.925194	-0.009525	-0.603667
51	6	C	-5.082733	0.096439	-1.322078
52	6	C	-6.251400	-0.196794	-0.545660
53	6	C	-5.966715	-0.522461	0.750006
54	16	S	-4.249026	-0.477354	1.042795
55	1	H	-5.106472	0.373370	-2.368529
56	1	H	-7.259448	-0.165763	-0.940574
57	1	H	-6.649666	-0.785738	1.544247
58	35	Br	-1.996087	0.276547	-1.239017

E(RB3LYP) = –4317.20454376 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction =	0.471023
Thermal correction to Energy =	0.487678
Thermal correction to Enthalpy	0.488296
Thermal correction to Gibbs Free Energy =	0.432527
Sum of electronic and zero-point Energies =	-4316.733521
Sum of electronic and thermal Energies =	-4316.716866
Sum of electronic and thermal Enthalpies =	-4316.716248
Sum of electronic and thermal Free Energies =	-4316.772017

Table C50. Cartesian coordinates and energies for Transition state **TS–2C (Cl)** found in Figure C6 and Figure 5.18. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	0.769602	0.296404	1.773208
2	6	C	3.763412	-3.458388	-1.288892
3	1	H	3.050813	-4.102390	-1.815192
4	1	H	4.715513	-3.994286	-1.228192
5	1	H	3.920909	-2.566588	-1.904892
6	6	C	3.236511	-3.077190	0.098908
7	1	H	3.107113	-3.979490	0.708808
8	1	H	3.978909	-2.459188	0.618508
9	6	C	1.900609	-2.312493	0.048908
10	1	H	1.164910	-2.929995	-0.484192
11	1	H	2.047106	-1.418493	-0.574692
12	6	C	1.331108	-1.911794	1.396408
13	1	H	2.053206	-1.302393	1.965908
14	1	H	1.054910	-2.768995	2.014908
15	3	Li	-0.193099	0.531402	-0.791292
16	6	C	1.332898	1.698006	0.218008
17	6	C	1.133595	3.070805	0.274108
18	6	C	2.231693	3.903708	-0.120192
19	6	C	3.328595	3.179211	-0.497792
20	16	S	2.988999	1.478810	-0.362792
21	1	H	0.189494	3.498903	0.601908
22	1	H	2.204890	4.987608	-0.121592
23	1	H	4.287994	3.544613	-0.836392
24	6	C	-3.410795	-0.928007	-0.827392
25	6	C	-2.745996	-0.459005	0.260308
26	6	C	-3.447599	0.585493	0.936708
27	6	C	-4.645399	0.892090	0.347808
28	16	S	-4.943297	-0.092011	-1.051492
29	1	H	-3.081500	1.086194	1.825208
30	1	H	-5.373401	1.631988	0.649308
31	1	H	-3.131893	-1.711206	-1.518092
32	17	Cl	-0.864794	-1.134300	0.864708

E(RB3LYP) = –1738.17588856 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.233169		
Thermal correction to Energy =		0.243469		
Thermal correction to Enthalpy		0.244087		
Thermal correction to Gibbs Free Energy =		0.203003		
Sum of electronic and zero-point Energies =		-1737.942719		
Sum of electronic and thermal Energies =		-1737.932419		
Sum of electronic and thermal Enthalpies =		-1737.931801		
Sum of electronic and thermal Free Energies =		-1737.972886		

Table C51. Cartesian coordinates and energies for Transition state **TS–2C (Br)** found in Figure C6 and Figure 5.18. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	6	C	-3.842499	-3.467307	1.412598
2	1	H	-3.104899	-3.925006	2.080698
3	1	H	-4.700998	-4.143109	1.351298
4	1	H	-4.182001	-2.538108	1.882798
5	6	C	-3.234500	-3.191406	0.032698
6	1	H	-2.924598	-4.135406	-0.432403
7	1	H	-3.997501	-2.760708	-0.627503
8	6	C	-2.025102	-2.240104	0.081098
9	1	H	-1.274001	-2.671602	0.758198
10	1	H	-2.353304	-1.306605	0.562498
11	6	C	-1.369702	-1.934403	-1.260803
12	1	H	-2.114003	-1.514804	-1.964203
13	1	H	-0.990901	-2.844402	-1.736603
14	3	Li	-0.140608	0.699400	0.986498
15	3	Li	-1.124907	0.264798	-1.600803
16	6	C	-1.683510	1.745697	-0.108903
17	6	C	-1.529012	3.099097	-0.376603
18	16	S	-3.338309	1.560893	0.485498
19	6	C	-2.659514	3.943895	-0.124803
20	1	H	-0.595713	3.503899	-0.760103
21	6	C	-3.735813	3.248893	0.353598
22	1	H	-2.669416	5.014895	-0.292703
23	1	H	-4.711013	3.628291	0.624598
24	6	C	3.296392	0.953906	-0.329803
25	6	C	2.834894	-0.297094	-0.056902
26	6	C	3.731096	-1.052293	0.762598
27	6	C	4.862394	-0.357991	1.094898
28	16	S	4.857991	1.239509	0.414298
29	1	H	3.541098	-2.067993	1.086898
30	1	H	5.699395	-0.684789	1.695398
31	1	H	2.840390	1.734006	-0.922603
32	35	Br	0.947096	-1.019798	-0.706803

E(RB3LYP) = –3852.11261188 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.232985
Thermal correction to Energy = 0.243280
Thermal correction to Enthalpy 0.243898
Thermal correction to Gibbs Free Energy = 0.202941
Sum of electronic and zero-point Energies = -3851.879627
Sum of electronic and thermal Energies = -3851.869331
Sum of electronic and thermal Enthalpies = -3851.868713
Sum of electronic and thermal Free Energies = -3851.909671

Table C52. Cartesian coordinates and energies for Transition state **TS–4C (Cl)** found in Figure C6 and Figure 5.19. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-1.349618	0.448630	0.685235
2	6	C	3.938870	2.368722	-0.824658
3	1	H	3.473319	2.955125	-0.025909
4	1	H	4.750143	2.967601	-1.249321
5	1	H	4.384340	1.482035	-0.361458
6	6	C	2.908356	1.972632	-1.887835
7	1	H	2.489146	2.871271	-2.356524
8	1	H	3.399475	1.410878	-2.691687
9	6	C	1.752167	1.125009	-1.321580
10	1	H	1.276114	1.696344	-0.516074
11	1	H	2.206009	0.257644	-0.823099
12	6	C	0.706163	0.698344	-2.341286
13	1	H	1.097876	0.008519	-3.096677
14	1	H	0.281631	1.562106	-2.858016
15	3	Li	0.433600	-1.098039	-0.777962
16	6	C	2.708270	-2.879174	-0.013843
17	8	O	1.912902	-2.355012	-1.103575
18	6	C	2.811135	-2.312798	-2.234411
19	6	C	4.166590	-1.856394	-1.662993
20	6	C	4.051381	-2.154612	-0.142734
21	1	H	2.175284	-2.685827	0.913528
22	1	H	2.818070	-3.961726	-0.153652
23	1	H	2.875748	-3.319144	-2.663813
24	1	H	2.388143	-1.636659	-2.974562
25	1	H	4.989329	-2.398555	-2.131606
26	1	H	4.323953	-0.791615	-1.840111
27	1	H	4.875934	-2.762796	0.232120
28	1	H	4.023761	-1.227448	0.431800
29	6	C	-1.047943	3.302810	-0.207288
30	8	O	-1.139002	2.351159	0.882585
31	6	C	-0.602530	2.992267	2.058461
32	6	C	0.599260	3.771868	1.535611
33	6	C	0.135545	4.236330	0.134434
34	1	H	-0.907359	2.727698	-1.120600
35	1	H	-1.992163	3.852636	-0.269851
36	1	H	-1.364599	3.653791	2.489056
37	1	H	-0.349607	2.211150	2.775023
38	1	H	0.871959	4.602438	2.188309
39	1	H	1.457096	3.101199	1.457636
40	1	H	-0.193354	5.276734	0.152933
41	1	H	0.936690	4.152703	-0.600850
42	6	C	0.184067	-0.854297	1.413676
43	6	C	-0.126493	-1.976311	2.169086
44	6	C	0.708085	-2.249843	3.303011
45	6	C	1.701705	-1.321464	3.456028
46	16	S	1.588029	-0.124782	2.198116
47	1	H	-0.957227	-2.627662	1.909354
48	1	H	0.576648	-3.096755	3.967292
49	1	H	2.468730	-1.281114	4.216723

50	6	C	-3.641081	-1.664691	-0.277989
51	6	C	-3.393332	-0.583036	-1.061195
52	6	C	-4.556937	0.205351	-1.314525
53	6	C	-5.681009	-0.301593	-0.719708
54	16	S	-5.339054	-1.753846	0.170645
55	1	H	-4.557692	1.108028	-1.913323
56	1	H	-6.690007	0.085171	-0.748406
57	1	H	-2.960109	-2.426451	0.074446
58	17	Cl	-1.501626	-0.049702	-1.684020

E(RB3LYP) = –2203.28056001 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.471290		
Thermal correction to Energy =		0.487699		
Thermal correction to Enthalpy		0.488317		
Thermal correction to Gibbs Free Energy =		0.433958		
Sum of electronic and zero-point Energies =		-2202.809270		
Sum of electronic and thermal Energies =		-2202.792861		
Sum of electronic and thermal Enthalpies =		-2202.792243		
Sum of electronic and thermal Free Energies =		-2202.846602		

Table C53. Cartesian coordinates and energies for Transition state **TS–4C (Br)** found in Figure C6 and Figure 5.19. Structure was optimised at the UB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	-4.121193	2.074162	-1.181857
2	1	H	-4.547422	1.182093	-0.711226
3	1	H	-4.920960	2.575111	-1.735433
4	1	H	-3.800706	2.744815	-0.378548
5	6	C	-2.944820	1.705147	-2.092501
6	1	H	-3.294470	1.067116	-2.913026
7	1	H	-2.537319	2.608518	-2.562465
8	6	C	-1.809157	0.978071	-1.346937
9	1	H	-2.266274	0.110428	-0.850597
10	1	H	-1.469828	1.620348	-0.526523
11	6	C	-0.620785	0.573380	-2.219023
12	1	H	-0.216092	1.451728	-2.729075
13	1	H	-0.905408	-0.147536	-2.995126
14	3	Li	0.957875	0.648066	1.016482
15	3	Li	-0.547058	-1.093644	-0.595517
16	6	C	-2.706826	-2.454025	-2.239911
17	8	O	-1.916848	-2.444396	-1.029824
18	6	C	-2.781748	-2.998560	-0.010772
19	6	C	-4.139355	-2.340770	-0.270554
20	6	C	-4.136963	-2.082355	-1.801916
21	1	H	-2.258416	-1.749966	-2.937984
22	1	H	-2.668298	-3.460466	-2.671615
23	1	H	-2.826539	-4.086332	-0.146356

24	1	H	-2.346344	-2.771913	0.959138
25	1	H	-4.965849	-2.976779	0.049904
26	1	H	-4.199276	-1.400524	0.279832
27	1	H	-4.874294	-2.692443	-2.325948
28	1	H	-4.352676	-1.036086	-2.021776
29	6	C	-0.114531	3.184360	2.143295
30	8	O	0.600472	2.531377	1.072803
31	6	C	0.602566	3.445613	-0.051313
32	6	C	-0.692203	4.280183	0.074314
33	6	C	-1.286737	3.863989	1.442394
34	1	H	-0.407699	2.419852	2.862361
35	1	H	0.549342	3.910174	2.628912
36	1	H	1.495792	4.074860	0.014065
37	1	H	0.656191	2.841424	-0.955177
38	1	H	-0.462184	5.346463	0.048448
39	1	H	-1.384187	4.068043	-0.741252
40	1	H	-1.673955	4.710370	2.011348
41	1	H	-2.095468	3.142811	1.309690
42	6	C	-0.528974	-0.771015	1.588548
43	6	C	-0.208322	-1.868932	2.374686
44	6	C	-1.117507	-2.198793	3.433710
45	6	C	-2.181257	-1.340241	3.494938
46	16	S	-2.042170	-0.139164	2.243684
47	1	H	0.683970	-2.462160	2.190248
48	1	H	-0.987137	-3.035043	4.111526
49	1	H	-3.011492	-1.352301	4.187163
50	6	C	3.926955	-1.498981	0.196625
51	6	C	3.655424	-0.489831	-0.674473
52	6	C	4.812415	0.289995	-0.990854
53	6	C	5.944319	-0.146131	-0.356894
54	16	S	5.623157	-1.524213	0.650586
55	1	H	4.801466	1.139177	-1.663515
56	1	H	6.946591	0.253767	-0.418305
57	1	H	3.258331	-2.240088	0.611179
58	35	Br	1.679302	-0.052347	-1.398970

E(RB3LYP) = –4317.21646328 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.471134
Thermal correction to Energy = 0.487764
Thermal correction to Enthalpy 0.488382
Thermal correction to Gibbs Free Energy = 0.433165
Sum of electronic and zero-point Energies = -4316.745329
Sum of electronic and thermal Energies = -4316.728699
Sum of electronic and thermal Enthalpies = -4316.728081
Sum of electronic and thermal Free Energies = -4316.783298

Table C54. Relative energy comparison (in kcal mol^{-1}) of the homodimer isomers for **Prod–2a**.

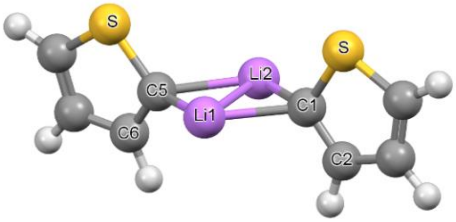
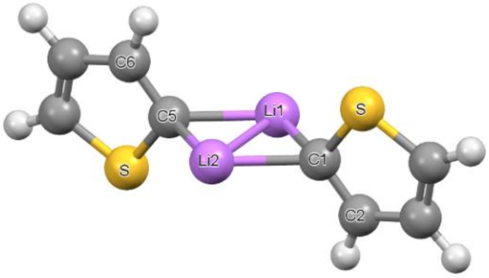
Structure:	**Prod–2a**	
Stereochemistry:	**Cis**	**Trans**
		
	Rel. Energies	
ΔG_{rel}	0.00	0.05
ΔH_{rel}	0.00	–0.01

Table C55. Relative energy comparison (in kcal mol^{-1}) of the homodimer isomers for **Prod–4a**.

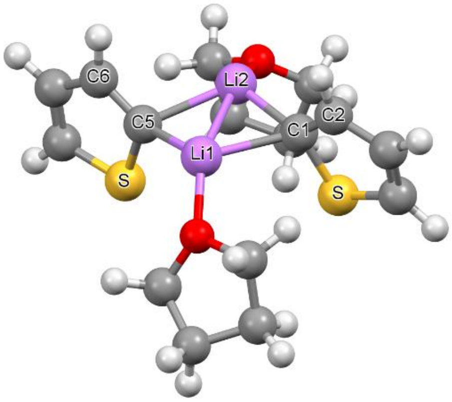
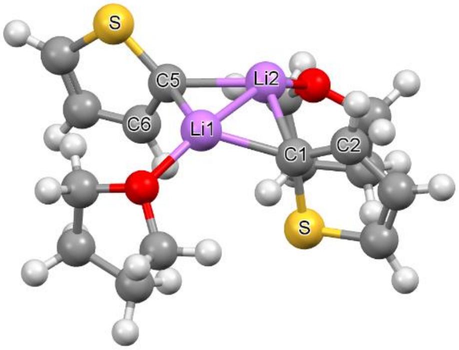
Structure:	**Prod–4a**	
Stereochemistry:	**Cis**	**Trans**
		
	Rel. Energies	
ΔG_{rel}	0.00	0.73
ΔH_{rel}	0.00	–0.03

Table C56. Relative energy comparison (in kcal mol^{-1}) of the homodimer isomers for **Prod–2b**.

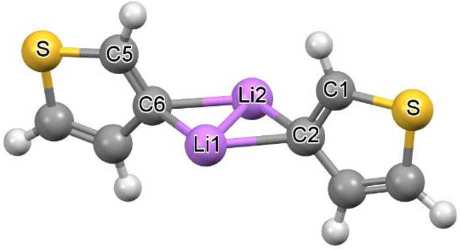
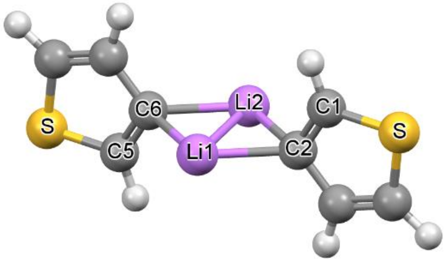
Structure:	**Prod–2b**	
Stereochemistry:	**Cis**	**Trans**
		
	Rel. Energies	
ΔG_{rel}	0.00	0.21
ΔH_{rel}	0.00	–0.05

Table C57. Relative energy comparison (in kcal mol^{-1}) of the homodimer isomers for **Prod–4b**.

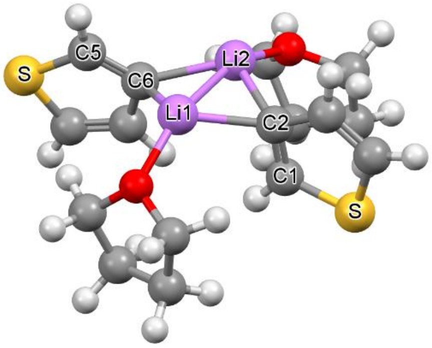
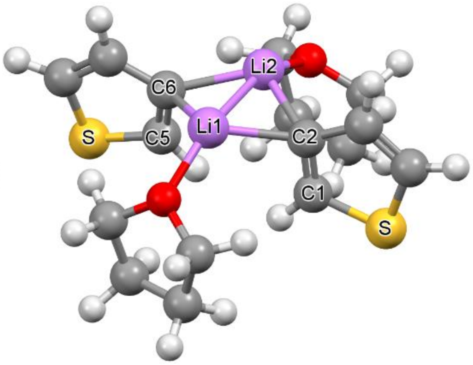
Structure:	**Prod–4b**	
Stereochemistry:	**Trans**	**Cis**
		
	Rel. Energies	
ΔG_{rel}	0.00	0.21
ΔH_{rel}	0.00	–0.16

Table C58. Relative energy comparison (in kcal mol^{-1}) and computed bond lengths (in Å) for the homodimer isomers for **Prod–2c/Prod–2d**.

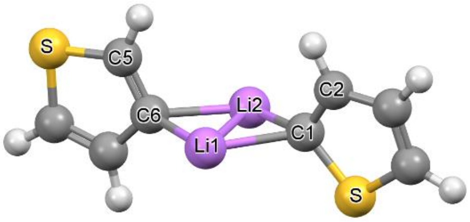
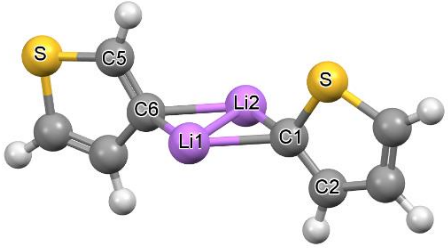
Structure:	**Prod–2c/Prod–2d**	
Stereochemistry:	**Trans**	**Cis**
		
	Rel. Energies	
ΔG_{rel}	0.00	0.12
ΔH_{rel}	0.00	0.01
Bond	Bond Length	
C(1)—S	1.7653	1.7662
C(1)—C(2)	1.3883	1.3883
C(1)—Li(1)	2.1998	2.1706
C(1)—Li(2)	2.1820	2.2045
C(1)– –C(6)	3.6389	3.6324
Li(1)– –Li(2)	2.4185	2.4231
C(6)—Li(1)	2.1723	2.1902
C(6)—Li(2)	2.1953	2.1674
C(6)—C(5)	1.3748	1.3747
C(5)—S	1.7703	1.7704

Table C59. Relative energy comparison (in kcal mol^{-1}) and computed bond lengths (in Å) for the homodimer isomers for **Prod–4c/Prod–4d**.

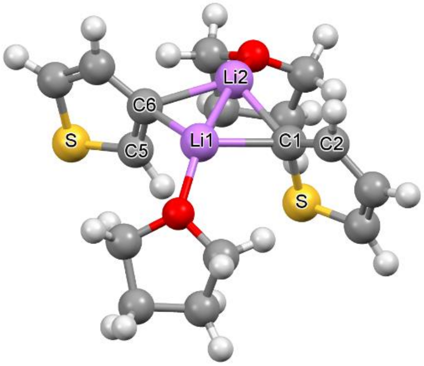
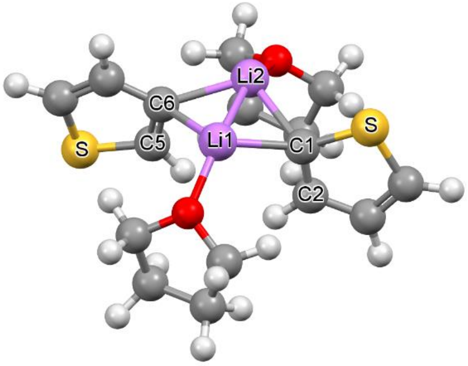
Structure:	**Prod–4c/Prod–4d**	
Stereochemistry:	**Cis**	**Trans**
		
	Rel. Energies	
ΔG_{rel}	0.00	0.04
ΔH_{rel}	0.00	0.11
Bond	Bond Length	
C(1)—S	1.7702	1.7586
C(1)—C(2)	1.3868	1.3874
C(1)—Li(1)	2.2264	2.1617
C(1)—Li(2)	2.1702	2.2040
C(1)– –C(6)	3.5405	3.5050
Li(1)– –Li(2)	2.4283	2.4262
C(6)—Li(1)	2.1678	2.1949
C(6)—Li(2)	2.1879	2.1767
C(6)—C(5)	1.3737	1.3734
C(5)—S	1.7700	1.7696

Table C60. Cartesian coordinates and energies for Product **Prod–1a** found in Figure 5.3 and Table 5.2. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	0.166787	0.896192	-1.168604
2	6	C	5.217492	-1.025696	-0.000604
3	1	H	4.999193	-1.637996	0.881196
4	1	H	6.291191	-0.812393	0.000496
5	1	H	5.000493	-1.635096	-0.884804
6	6	C	4.377388	0.256902	0.000796
7	1	H	4.631387	0.864903	0.878796
8	1	H	4.632387	0.867603	-0.875004
9	6	C	2.858089	0.006098	-0.000304
10	1	H	2.626591	-0.628902	0.870296
11	1	H	2.627491	-0.626302	-0.873004
12	6	C	1.951086	1.256696	0.001096
13	1	H	2.249684	1.884597	-0.862304
14	1	H	2.249284	1.882297	0.866196
15	3	Li	0.163787	0.900392	1.168896
16	6	C	-1.640112	0.435587	-0.001804
17	6	C	-2.764914	1.249285	-0.001604
18	6	C	-4.041712	0.595382	-0.000004
19	6	C	-3.933809	-0.767918	0.001196
20	16	S	-2.252208	-1.220814	0.000296
21	1	H	-2.686517	2.333785	-0.002804
22	1	H	-4.992814	1.116379	0.000296
23	1	H	-4.725807	-1.503620	0.002396

E(RB3LYP) = –725.495870476 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.175978
Thermal correction to Energy = 0.182871
Thermal correction to Enthalpy 0.183489
Thermal correction to Gibbs Free Energy = 0.151783
Sum of electronic and zero-point Energies = -725.319893
Sum of electronic and thermal Energies = -725.312999
Sum of electronic and thermal Enthalpies = -725.312381
Sum of electronic and thermal Free Energies = -725.344088

Table C61. Cartesian coordinates and energies for Product **Prod–3a** found in Figure 5.5 and Table 5.2. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	C	1.089032	-3.769787	1.238111
2	1	H	1.832428	-3.157783	1.760711
3	1	H	1.376839	-4.818886	1.360111
4	1	H	0.131231	-3.626194	1.750211
5	6	C	0.987929	-3.366388	-0.237589
6	1	H	1.947430	-3.548682	-0.738889
7	1	H	0.253933	-4.003693	-0.747589
8	6	C	0.594920	-1.893891	-0.446489
9	1	H	1.325516	-1.277486	0.097311
10	1	H	-0.349581	-1.723097	0.092211
11	6	C	0.469717	-1.399891	-1.903889
12	1	H	-0.243279	-2.062996	-2.429289
13	1	H	1.426318	-1.599885	-2.419689
14	3	Li	-1.150593	-0.004502	-1.697089
15	3	Li	1.114003	0.677413	-1.677689
16	6	C	3.827009	-0.306270	-0.779289
17	8	O	2.887302	0.789624	-0.863589
18	6	C	3.139497	1.634826	0.279111
19	6	C	3.367703	0.647627	1.421011
20	6	C	4.081011	-0.539968	0.727611
21	1	H	3.379215	-1.159472	-1.286689
22	1	H	4.745908	-0.019464	-1.301489
23	1	H	4.030393	2.245632	0.085111
24	1	H	2.270193	2.277920	0.408811
25	1	H	3.955200	1.080031	2.232411
26	1	H	2.403305	0.333321	1.825611
27	1	H	5.151711	-0.542161	0.938811
28	1	H	3.673417	-1.496371	1.056511
29	6	C	-3.454192	-0.075617	0.148311
30	8	O	-2.771488	-0.756812	-0.927089
31	6	C	-2.999478	-2.171914	-0.732689
32	6	C	-3.144977	-2.378615	0.792311
33	6	C	-3.163886	-0.942015	1.370711
34	1	H	-3.048299	0.933186	0.209811
35	1	H	-4.527292	-0.034124	-0.077389
36	1	H	-3.912977	-2.455720	-1.265789
37	1	H	-2.152975	-2.700508	-1.169489
38	1	H	-4.069274	-2.912921	1.018711
39	1	H	-2.315673	-2.960109	1.196611
40	1	H	-3.907387	-0.811720	2.158611
41	1	H	-2.184888	-0.675609	1.773711
42	6	C	-0.436904	1.760703	-0.588289
43	6	C	-0.425203	1.594203	0.789611
44	6	C	-0.960610	2.665099	1.578411
45	6	C	-1.409017	3.707896	0.813911
46	16	S	-1.154914	3.340998	-0.872289
47	1	H	-0.038597	0.689005	1.249811
48	1	H	-1.011610	2.657399	2.661811
49	1	H	-1.854623	4.637194	1.140511

E(RB3LYP) = –1190.59699774 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =	0.413747			
Thermal correction to Energy =	0.426896			
Thermal correction to Enthalpy	0.427514			
Thermal correction to Gibbs Free Energy =	0.380358			
Sum of electronic and zero-point Energies =	-1190.183251			
Sum of electronic and thermal Energies =	-1190.170102			
Sum of electronic and thermal Enthalpies =	-1190.169484			
Sum of electronic and thermal Free Energies =	-1190.216640			

Table C62. Cartesian coordinates and energies for Product **Prod–1b** found in Figure 5.7 and Table 5.3. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	-0.269388	1.004003	1.162801
2	6	C	-5.298085	-1.126202	-0.000599
3	1	H	-5.066585	-1.730902	-0.884399
4	1	H	-6.376586	-0.938503	0.000101
5	1	H	-5.065685	-1.732801	0.881601
6	6	C	-4.488487	0.175899	0.000401
7	1	H	-4.758087	0.779999	-0.875699
8	1	H	-4.757287	0.778099	0.878001
9	6	C	-2.963587	-0.038099	-0.000599
10	1	H	-2.717786	-0.664599	-0.873199
11	1	H	-2.716886	-0.666699	0.870201
12	6	C	-2.088188	1.234502	0.000501
13	1	H	-2.404688	1.851901	0.865801
14	1	H	-2.405588	1.854101	-0.862899
15	3	Li	-0.269488	1.003603	-1.162099
16	6	C	1.852914	-0.798294	0.001101
17	6	C	1.532013	0.538205	0.000701
18	6	C	2.770612	1.295206	-0.000599
19	6	C	3.928113	0.561908	-0.000999
20	16	S	3.591515	-1.140393	0.000001
21	1	H	2.803611	2.381407	-0.001099
22	1	H	4.951212	0.912509	-0.001899
23	1	H	1.194915	-1.659795	0.001901

E(RB3LYP) = –725.483489599 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =	0.175315			
Thermal correction to Energy =	0.182394			
Thermal correction to Enthalpy	0.183012			
Thermal correction to Gibbs Free Energy =	0.150579			
Sum of electronic and zero-point Energies =	-725.308175			
Sum of electronic and thermal Energies =	-725.301096			
Sum of electronic and thermal Enthalpies =	-725.300478			
Sum of electronic and thermal Free Energies =	-725.332910			

Table C63. Cartesian coordinates and energies for Product **Prod–3b** found in Figure 5.8 and Table 5.3. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-1.136592	-0.151911	1.815704
2	6	C	1.133948	-3.640785	-1.494496
3	1	H	0.168046	-3.473896	-1.984096
4	1	H	1.442959	-4.668382	-1.710496
5	1	H	1.858940	-2.968877	-1.967296
6	6	C	1.038945	-3.370286	0.011704
7	1	H	0.325052	-4.066494	0.470604
8	1	H	2.007647	-3.572775	0.487104
9	6	C	0.614828	-1.930691	0.350204
10	1	H	-0.339174	-1.738602	-0.163496
11	1	H	1.325520	-1.253883	-0.146896
12	6	C	0.493324	-1.563793	1.845604
13	1	H	1.454527	-1.802682	2.336604
14	1	H	-0.211068	-2.276601	2.314304
15	3	Li	1.114500	0.526715	1.814004
16	6	C	3.111187	1.678737	-0.089596
17	8	O	2.863798	0.727034	0.966504
18	6	C	3.812710	-0.349455	0.784504
19	6	C	4.089611	-0.426852	-0.734596
20	6	C	3.355297	0.805840	-1.317396
21	1	H	2.235680	2.322227	-0.162196
22	1	H	3.994380	2.278747	0.164804
23	1	H	4.722007	-0.113544	1.347304
24	1	H	3.362520	-1.251960	1.195304
25	1	H	5.162311	-0.380639	-0.930396
26	1	H	3.711822	-1.356056	-1.162696
27	1	H	3.934391	1.321347	-2.085096
28	1	H	2.396600	0.513029	-1.750996
29	6	C	-2.997768	-2.226532	0.702804
30	8	O	-2.782984	-0.831530	1.021604
31	6	C	-3.463893	-0.065238	0.003604
32	6	C	-3.155385	-0.819534	-1.285996
33	6	C	-3.141768	-2.300734	-0.835096
34	1	H	-2.145762	-2.783323	1.091304
35	1	H	-3.907865	-2.564943	1.208904
36	1	H	-4.539193	-0.053450	0.222504
37	1	H	-3.068705	0.949067	0.033504
38	1	H	-3.887587	-0.620442	-2.069896
39	1	H	-2.171188	-0.517623	-1.649596
40	1	H	-4.068562	-2.808744	-1.107296
41	1	H	-2.314861	-2.849124	-1.287696
42	6	C	-0.417912	1.637397	-0.388996
43	6	C	-0.484414	1.773996	0.975404
44	6	C	-1.102029	3.052889	1.268004
45	6	C	-1.470537	3.808985	0.185604
46	16	S	-1.079928	3.003690	-1.303096
47	1	H	-1.276333	3.412187	2.278604
48	1	H	-1.939748	4.783380	0.167904
49	1	H	-0.030603	0.810902	-0.972596

E(RB3LYP) = –1190.58510818 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.413302		
Thermal correction to Energy =		0.426487		
Thermal correction to Enthalpy		0.427105		
Thermal correction to Gibbs Free Energy =		0.380197		
Sum of electronic and zero-point Energies =		-1190.171806		
Sum of electronic and thermal Energies =		-1190.158621		
Sum of electronic and thermal Enthalpies =		-1190.158003		
Sum of electronic and thermal Free Energies =		-1190.204911		

Table C64. Cartesian coordinates and energies for Product **Prod–2a (Cis)** found in Figure 5.10, Table 5.4 and Table C54. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	-0.042112	0.219201	1.224685
2	3	Li	0.042488	0.219901	-1.223315
3	6	C	-1.809312	0.256797	-0.097815
4	6	C	-2.658815	1.349396	0.013585
5	16	S	-2.858210	-1.163805	-0.094415
6	6	C	-4.064314	1.074993	0.094385
7	1	H	-2.281217	2.368696	0.037585
8	6	C	-4.341211	-0.263308	0.048285
9	1	H	-4.829716	1.837991	0.182885
10	1	H	-5.305310	-0.750510	0.088785
11	6	C	1.809388	0.257405	0.097785
12	6	C	2.659485	1.349607	-0.013615
13	6	C	4.064886	1.074409	-0.094515
14	6	C	4.341089	-0.263990	-0.048415
15	16	S	2.857590	-1.163693	0.094285
16	1	H	2.282383	2.369106	-0.037515
17	1	H	4.830584	1.837111	-0.182915
18	1	H	5.304890	-0.751588	-0.088915

E(RB3LYP) = –1120.10124467 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.112252		
Thermal correction to Energy =		0.118641		
Thermal correction to Enthalpy		0.119259		
Thermal correction to Gibbs Free Energy =		0.087736		
Sum of electronic and zero-point Energies =		-1119.988992		
Sum of electronic and thermal Energies =		-1119.982604		
Sum of electronic and thermal Enthalpies =		-1119.981986		
Sum of electronic and thermal Free Energies =		-1120.013509		

Table C65. Cartesian coordinates and energies for Product **Prod–2a (Trans)** found in Figure 5.10 and Table C54. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-0.032713	-0.112514	-1.219300
2	3	Li	0.032387	0.111986	1.220000
3	6	C	1.808287	0.138290	-0.080300
4	6	C	2.561184	1.304792	-0.054000
5	16	S	2.974590	-1.183807	-0.010700
6	6	C	3.986084	1.156896	0.015400
7	1	H	2.097381	2.287791	-0.085200
8	6	C	4.376787	-0.153103	0.045100
9	1	H	4.683782	1.986598	0.041700
10	1	H	5.379988	-0.552701	0.094100
11	6	C	-1.808413	-0.138719	0.081300
12	6	C	-2.561610	-1.304921	0.055700
13	6	C	-3.986510	-1.156624	-0.014800
14	6	C	-4.376713	0.153575	-0.046100
15	16	S	-2.974116	1.183778	0.009600
16	1	H	-2.098207	-2.288019	0.088000
17	1	H	-4.684408	-1.986126	-0.040700
18	1	H	-5.379714	0.553372	-0.096200

E(RB3LYP) = –1120.10126433 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.112310
Thermal correction to Energy = 0.118649
Thermal correction to Enthalpy 0.119267
Thermal correction to Gibbs Free Energy = 0.087829
Sum of electronic and zero-point Energies = -1119.988954
Sum of electronic and thermal Energies = -1119.982615
Sum of electronic and thermal Enthalpies = -1119.981997
Sum of electronic and thermal Free Energies = -1120.013436

Table C66. Cartesian coordinates and energies for Product **Prod–4a (Cis)** found in Figure 5.12, Table 5.4 and Table C55. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	0.836381	-0.806409	1.255303
2	3	Li	-1.033108	0.795003	1.319203
3	6	C	-3.687007	1.076419	0.031503
4	8	O	-2.506702	1.769212	0.511703
5	6	C	-2.239995	2.824510	-0.436597
6	6	C	-2.476200	2.160712	-1.790297
7	6	C	-3.660606	1.203419	-1.508297
8	1	H	-3.629013	0.050319	0.390003

9	1	H	-4.569703	1.562025	0.460803
10	1	H	-2.939490	3.651615	-0.260897
11	1	H	-1.219393	3.168504	-0.273797
12	1	H	-2.691695	2.884313	-2.577897
13	1	H	-1.584803	1.597106	-2.075797
14	1	H	-4.601703	1.617925	-1.874597
15	1	H	-3.509412	0.232718	-1.980097
16	6	C	3.644880	-0.998327	0.335703
17	8	O	2.365076	-1.678819	0.449803
18	6	C	2.221070	-2.644218	-0.631897
19	6	C	3.548270	-2.621527	-1.393597
20	6	C	4.068979	-1.204230	-1.112397
21	1	H	3.495487	0.044174	0.614203
22	1	H	4.351177	-1.465332	1.031503
23	1	H	1.983364	-3.616517	-0.196297
24	1	H	1.384172	-2.325413	-1.258897
25	1	H	4.237965	-3.365431	-0.985197
26	1	H	3.411869	-2.829226	-2.455897
27	1	H	5.147180	-1.106537	-1.248197
28	1	H	3.567684	-0.472927	-1.752197
29	6	C	1.019196	1.410589	1.045103
30	6	C	1.952299	2.008083	1.879703
31	6	C	2.983804	2.786377	1.255103
32	6	C	2.871205	2.809978	-0.107697
33	16	S	1.488599	1.870086	-0.596597
34	1	H	1.911399	1.889384	2.959603
35	1	H	3.770708	3.300672	1.795603
36	1	H	3.502608	3.316474	-0.824097
37	6	C	-1.227722	-1.405596	1.048503
38	6	C	-2.222325	-1.901790	1.879103
39	6	C	-3.271030	-2.661183	1.260303
40	6	C	-3.108531	-2.774784	-0.092997
41	16	S	-1.659526	-1.940094	-0.579497
42	1	H	-2.215524	-1.721190	2.951303
43	1	H	-4.104433	-3.099478	1.798203
44	1	H	-3.738134	-3.292580	-0.802897

E(RB3LYP) = –1585.20180079 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.349188

Thermal correction to Energy = 0.361945

Thermal correction to Enthalpy 0.362563

Thermal correction to Gibbs Free Energy = 0.315076

Sum of electronic and zero-point Energies = -1584.852612

Sum of electronic and thermal Energies = -1584.839856

Sum of electronic and thermal Enthalpies = -1584.839238

Sum of electronic and thermal Free Energies = -1584.886725

Table C67. Cartesian coordinates and energies for Product **Prod–4a (Trans)** found in Figure 5.12 and Table C55. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	-0.895703	0.801906	-1.321908
2	3	Li	0.758698	-1.013292	-1.313608
3	6	C	1.809299	-2.914992	0.674892
4	8	O	2.139699	-2.067392	-0.446008
5	6	C	3.457498	-1.512091	-0.190608
6	6	C	3.640898	-1.517490	1.343992
7	6	C	2.331899	-2.139891	1.879092
8	1	H	0.730099	-3.065193	0.665792
9	1	H	2.317000	-3.881291	0.560992
10	1	H	4.200599	-2.141890	-0.689808
11	1	H	3.477297	-0.514491	-0.627508
12	1	H	4.504599	-2.124090	1.623592
13	1	H	3.793497	-0.509090	1.728292
14	1	H	2.487999	-2.775891	2.751992
15	1	H	1.616998	-1.356992	2.143092
16	6	C	-1.770805	3.152506	0.218192
17	8	O	-2.209804	2.037705	-0.586908
18	6	C	-3.401104	1.525105	0.058192
19	6	C	-3.177604	1.723905	1.571692
20	6	C	-1.945705	2.663306	1.655892
21	1	H	-0.740805	3.376006	-0.057708
22	1	H	-2.406406	4.020705	0.002992
23	1	H	-4.262204	2.099204	-0.301108
24	1	H	-3.509903	0.482105	-0.234708
25	1	H	-4.059304	2.167504	2.037392
26	1	H	-2.979203	0.770205	2.061092
27	1	H	-2.086605	3.488206	2.356092
28	1	H	-1.056904	2.106706	1.959692
29	6	C	1.218896	1.172108	-1.127308
30	6	C	2.218396	1.611809	-1.982608
31	6	C	3.339796	2.281109	-1.387108
32	6	C	3.231595	2.378709	-0.027208
33	16	S	1.743496	1.639808	0.494892
34	1	H	2.161696	1.453708	-3.056808
35	1	H	4.184195	2.669510	-1.945908
36	1	H	3.921295	2.834110	0.669292
37	6	C	-1.314202	-1.283394	-0.789608
38	6	C	-1.579902	-1.414194	0.566592
39	6	C	-2.762101	-2.140195	0.928792
40	6	C	-3.451601	-2.596495	-0.160908
41	16	S	-2.619001	-2.121795	-1.617308
42	1	H	-0.933502	-0.975394	1.323192
43	1	H	-3.084001	-2.309695	1.950392
44	1	H	-4.368001	-3.169396	-0.183608

E(RB3LYP) = –1585.20210954 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.349570	
Thermal correction to Energy =	0.362198	
Thermal correction to Enthalpy	0.362816	
Thermal correction to Gibbs Free Energy =	0.316544	
Sum of electronic and zero-point Energies =	-1584.852540	
Sum of electronic and thermal Energies =	-1584.839911	
Sum of electronic and thermal Enthalpies =	-1584.839293	
Sum of electronic and thermal Free Energies =	-1584.885565	

Table C68. Cartesian coordinates and energies for Product **Prod–2b (Cis)** found in Figure 5.14, Table 5.5 and Table C56. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	0.047619	0.266405	1.206390
2	3	Li	-0.044681	0.233505	-1.192910
3	6	C	2.515518	-0.944296	0.009590
4	6	C	1.820019	0.237805	-0.085110
5	6	C	2.784519	1.322504	-0.114910
6	6	C	4.104219	0.959904	-0.048710
7	16	S	4.276118	-0.762897	0.059090
8	1	H	2.501120	2.369204	-0.184710
9	1	H	4.980919	1.593103	-0.055410
10	1	H	2.136218	-1.958796	0.055490
11	6	C	-2.526082	-0.954493	0.003190
12	6	C	-1.818181	0.219806	0.101490
13	6	C	-2.770681	1.315707	0.115490
14	6	C	-4.093681	0.968307	0.035490
15	16	S	-4.283882	-0.752893	-0.067510
16	1	H	-2.475980	2.359507	0.184090
17	1	H	-4.962881	1.611708	0.029590
18	1	H	-2.157882	-1.973294	-0.033910

E(RB3LYP) = –1120.07662915 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.111758	
Thermal correction to Energy =	0.118233	
Thermal correction to Enthalpy	0.118851	
Thermal correction to Gibbs Free Energy =	0.086140	
Sum of electronic and zero-point Energies =	-1119.964871	
Sum of electronic and thermal Energies =	-1119.958396	
Sum of electronic and thermal Enthalpies =	-1119.957778	
Sum of electronic and thermal Free Energies =	-1119.990489	

Table C69. Cartesian coordinates and energies for Product **Prod–2b (Trans)** found in Figure 5.14 and Table C56. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	0.013097	-0.039113	1.192285
2	3	Li	-0.013003	0.040187	-1.189915
3	6	C	2.610200	-0.950703	-0.016915
4	6	C	1.824096	0.177294	-0.018715
5	6	C	2.700991	1.333998	-0.002815
6	6	C	4.045792	1.072303	0.008885
7	16	S	4.352299	-0.635196	0.002385
8	1	H	2.335987	2.357496	-0.000115
9	1	H	4.870890	1.771306	0.021085
10	1	H	2.311205	-1.992704	-0.026515
11	6	C	-2.610807	0.951077	0.016385
12	6	C	-1.824003	-0.176420	0.020985
13	6	C	-2.700198	-1.333724	0.005585
14	6	C	-4.045199	-1.072729	-0.008415
15	16	S	-4.352706	0.634570	-0.004915
16	1	H	-2.334694	-2.356922	0.004885
17	1	H	-4.869896	-1.772232	-0.020815
18	1	H	-2.312511	1.993278	0.024985

E(RB3LYP) = –1120.07661529 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.111618
Thermal correction to Energy = 0.118144
Thermal correction to Enthalpy 0.118762
Thermal correction to Gibbs Free Energy = 0.086468
Sum of electronic and zero-point Energies = -1119.964998
Sum of electronic and thermal Energies = -1119.958471
Sum of electronic and thermal Enthalpies = -1119.957853
Sum of electronic and thermal Free Energies = -1119.990148

Table C70. Cartesian coordinates and energies for Product **Prod–4b (Cis)** found in Figure 5.15, Table 5.5 and Table C57. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	-0.653287	-1.014808	1.581105
2	3	Li	0.653591	1.016407	1.581405
3	6	C	1.087064	3.513811	0.036605
4	8	O	1.708576	2.409518	0.732305
5	6	C	2.905180	2.088631	-0.009695
6	6	C	2.475779	2.187626	-1.473795
7	6	C	1.375267	3.281814	-1.461095

8	1	H	0.027164	3.498700	0.287205
9	1	H	1.536254	4.447816	0.392405
10	1	H	3.682872	2.822539	0.236705
11	1	H	3.227590	1.093735	0.294205
12	1	H	3.312076	2.434835	-2.129595
13	1	H	2.063489	1.229222	-1.793195
14	1	H	1.711657	4.204518	-1.936895
15	1	H	0.479070	2.944505	-1.983595
16	6	C	-1.085459	-3.512412	0.036705
17	8	O	-1.707771	-2.408219	0.731905
18	6	C	-2.903875	-2.087732	-0.011095
19	6	C	-2.473474	-2.186927	-1.474995
20	6	C	-1.372262	-3.280416	-1.461295
21	1	H	-0.025760	-3.497201	0.288205
22	1	H	-1.534849	-4.446417	0.392005
23	1	H	-3.681567	-2.821641	0.234905
24	1	H	-3.226686	-1.092836	0.292405
25	1	H	-3.309271	-2.435037	-2.130995
26	1	H	-2.061684	-1.228423	-1.794595
27	1	H	-1.707452	-4.203219	-1.937595
28	1	H	-0.475766	-2.942206	-1.982695
29	6	C	-1.587610	1.175282	-0.196595
30	6	C	-1.473608	0.986483	1.158905
31	6	C	-2.709813	1.425770	1.777105
32	6	C	-3.674318	1.903059	0.927905
33	16	S	-3.133818	1.858665	-0.721795
34	1	H	-2.887013	1.385068	2.848305
35	1	H	-4.660222	2.279149	1.165205
36	1	H	-0.869908	0.958490	-0.979095
37	6	C	1.586715	-1.172983	-0.195695
38	6	C	1.474113	-0.984985	1.160105
39	6	C	2.709218	-1.428371	1.777205
40	6	C	3.671923	-1.907561	0.927205
41	16	S	3.130723	-1.860167	-0.722195
42	1	H	2.887017	-1.389069	2.848405
43	1	H	4.656927	-2.286750	1.163605
44	1	H	0.869213	-0.953491	-0.977495

E(RB3LYP) = –1585.17804326 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.349782		
Thermal correction to Energy =		0.362214		
Thermal correction to Enthalpy		0.362832		
Thermal correction to Gibbs Free Energy =		0.317219		
Sum of electronic and zero-point Energies =		-1584.828261		
Sum of electronic and thermal Energies =		-1584.815829		
Sum of electronic and thermal Enthalpies =		-1584.815211		
Sum of electronic and thermal Free Energies =		-1584.860825		

Table C71. Cartesian coordinates and energies for Product **Prod–4b (Trans)** found in Figure 5.15 and Table C57. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	-0.825301	0.828416	-1.469178
2	3	Li	0.522516	-1.167999	-1.396961
3	6	C	1.335887	-3.373936	0.375767
4	8	O	1.767105	-2.469414	-0.662151
5	6	C	3.124605	-2.071401	-0.338679
6	6	C	3.251268	-2.173669	1.198039
7	6	C	1.892528	-2.755366	1.654884
8	1	H	0.248062	-3.429186	0.335517
9	1	H	1.759363	-4.368939	0.188929
10	1	H	3.815047	-2.750990	-0.848425
11	1	H	3.260835	-1.059801	-0.717510
12	1	H	4.075040	-2.835922	1.470802
13	1	H	3.440183	-1.196747	1.642974
14	1	H	1.990487	-3.483403	2.461701
15	1	H	1.228292	-1.956784	1.993360
16	6	C	-1.051919	3.425181	-0.101154
17	8	O	-1.785456	2.293039	-0.625525
18	6	C	-2.839650	2.020571	0.323938
19	6	C	-2.160064	2.179392	1.683132
20	6	C	-1.110294	3.293250	1.435862
21	1	H	-0.042145	3.370009	-0.505118
22	1	H	-1.537918	4.344294	-0.445965
23	1	H	-3.644278	2.753290	0.182710
24	1	H	-3.217304	1.018721	0.125913
25	1	H	-2.869943	2.432025	2.472357
26	1	H	-1.672364	1.240104	1.950677
27	1	H	-1.408116	4.238757	1.892321
28	1	H	-0.136357	3.016185	1.840820
29	6	C	-2.753504	-1.365111	-1.526232
30	6	C	-1.575192	-1.156831	-0.854244
31	6	C	-1.815619	-1.406293	0.556650
32	6	C	-3.089657	-1.774514	0.899142
33	16	S	-4.117292	-1.845171	-0.497110
34	1	H	-1.048000	-1.303073	1.318713
35	1	H	-3.487769	-2.003673	1.878290
36	1	H	-2.963972	-1.274507	-2.585509
37	6	C	1.563132	1.040304	0.153882
38	6	C	1.324243	0.867264	-1.187133
39	6	C	2.441969	1.429799	-1.918824
40	6	C	3.444218	1.979071	-1.161840
41	16	S	3.089289	1.852417	0.533445
42	1	H	2.506635	1.424768	-3.003422
43	1	H	4.361076	2.449714	-1.489924
44	1	H	0.954644	0.742707	1.000089

E(RB3LYP) =	–1585.17757343	Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.349410	
Thermal correction to Energy =	0.361995	
Thermal correction to Enthalpy	0.362613	
Thermal correction to Gibbs Free Energy =	0.316409	
Sum of electronic and zero-point Energies =	-1584.818164	
Sum of electronic and thermal Energies =	-1584.815578	
Sum of electronic and thermal Enthalpies =	-1584.814960	
Sum of electronic and thermal Free Energies =	-1584.861164	

Table C72. Cartesian coordinates and energies for Product **Prod–2c/Prod–2d (Cis)** found in Figure 5.18, Figure 5.20 and Table C58. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	**Atomic Number**	**Atomic Type**	**Coordinates (Angstroms)**		
			X	**Y**	**Z**
1	3	Li	0.064906	0.234395	-1.202608
2	3	Li	0.138806	0.260295	1.219192
3	6	C	-2.417495	-0.919905	0.086492
4	6	C	-1.707494	0.257295	0.083892
5	6	C	-2.657194	1.352296	-0.000108
6	6	C	-3.980594	1.001596	-0.054708
7	16	S	-4.174295	-0.721504	-0.006208
8	1	H	-2.360194	2.397395	-0.021008
9	1	H	-4.848394	1.643496	-0.120208
10	1	H	-2.051295	-1.938905	0.136092
11	6	C	1.921306	0.247394	-0.077908
12	6	C	2.795406	1.324094	-0.015108
13	6	C	4.196206	1.022393	0.049992
14	6	C	4.444705	-0.322307	0.040392
15	16	S	2.940705	-1.194606	-0.049308
16	1	H	2.439506	2.351594	-0.015708
17	1	H	4.978606	1.771293	0.101592
18	1	H	5.399005	-0.828307	0.080092

E(RB3LYP) =	–1120.08899108	Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.112118	
Thermal correction to Energy =	0.118483	
Thermal correction to Enthalpy	0.119101	
Thermal correction to Gibbs Free Energy =	0.087456	
Sum of electronic and zero-point Energies =	-1119.976873	
Sum of electronic and thermal Energies =	-1119.970508	
Sum of electronic and thermal Enthalpies =	-1119.969890	
Sum of electronic and thermal Free Energies =	-1120.001535	

Table C73. Cartesian coordinates and energies for Product **Prod–2c/Prod–2d (Trans)** found in Figure 5.18, Figure 5.20 and Table C58. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	-0.135210	-0.126703	-1.205916
2	3	Li	-0.063510	-0.219902	1.209684
3	6	C	2.435686	0.937706	0.004284
4	6	C	1.716590	-0.231397	-0.075016
5	6	C	2.658393	-1.335793	-0.095716
6	6	C	3.985192	-0.999089	-0.037416
7	16	S	4.192087	0.721112	0.049884
8	1	H	2.353297	-2.377094	-0.152716
9	1	H	4.848995	-1.649886	-0.039216
10	1	H	2.076583	1.959905	0.040684
11	6	C	-1.903311	0.104692	0.082284
12	6	C	-2.586015	1.310889	0.001784
13	6	C	-4.017115	1.244485	-0.070416
14	6	C	-4.484911	-0.040117	-0.047316
15	16	S	-3.146507	-1.148412	0.062284
16	1	H	-2.065018	2.265191	-0.006316
17	1	H	-4.664318	2.111983	-0.136616
18	1	H	-5.509710	-0.381720	-0.086616

E(RB3LYP) = –1120.08894752 Hartree

Thermochemistry: Temperature: 195.15 Kelvin Pressure: 1.000000 Atm

Zero-point correction = 0.112017

Thermal correction to Energy = 0.118423

Thermal correction to Enthalpy 0.119041

Thermal correction to Gibbs Free Energy = 0.087219

Sum of electronic and zero-point Energies = -1119.976931

Sum of electronic and thermal Energies = -1119.970524

Sum of electronic and thermal Enthalpies = -1119.969906

Sum of electronic and thermal Free Energies = -1120.001729

Table C74. Cartesian coordinates and energies for Product **Prod–4c/Prod–4d (Cis)** found in Figure 5.19, Figure 5.21 and Table C59. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	1.056024	-0.685867	1.499490
2	3	Li	-1.031005	0.555084	1.469690
3	6	C	-3.665904	0.525724	0.154690
4	8	O	-2.628023	1.358548	0.729690
5	6	C	-2.571052	2.623049	0.005990
6	6	C	-3.524849	2.476927	-1.191310
7	6	C	-3.721814	0.955722	-1.303710

8	1	H	-3.379380	-0.513870	0.309590
9	1	H	-4.613209	0.724702	0.670590
10	1	H	-2.865271	3.427142	0.684990
11	1	H	-1.532456	2.772073	-0.294410
12	1	H	-4.480060	2.965205	-0.981910
13	1	H	-3.109959	2.921136	-2.097210
14	1	H	-4.660008	0.680101	-1.788010
15	1	H	-2.896103	0.492941	-1.850410
16	6	C	3.655024	-0.674608	0.109590
17	8	O	2.668942	-1.488030	0.783090
18	6	C	2.650172	-2.752231	0.083990
19	6	C	2.864564	-2.405926	-1.401210
20	6	C	3.439030	-0.963013	-1.378710
21	1	H	3.477800	0.362488	0.391490
22	1	H	4.653431	-0.982985	0.443590
23	1	H	3.460386	-3.379312	0.473390
24	1	H	1.691383	-3.225653	0.292590
25	1	H	3.547880	-3.115110	-1.871210
26	1	H	1.918164	-2.438748	-1.942310
27	1	H	4.365628	-0.867991	-1.947010
28	1	H	2.716314	-0.254429	-1.785510
29	6	C	-0.844955	-1.618111	1.022990
30	6	C	-1.778036	-2.434033	1.644990
31	6	C	-2.574316	-3.278351	0.800790
32	6	C	-2.270520	-3.133444	-0.524910
33	16	S	-1.000847	-1.955315	-0.707810
34	1	H	-1.908536	-2.431936	2.724290
35	1	H	-3.336201	-3.958869	1.164990
36	1	H	-2.706008	-3.644054	-1.372310
37	6	C	0.993871	1.620131	-0.263410
38	6	C	0.903774	1.459429	1.097890
39	6	C	1.758452	2.448449	1.724490
40	6	C	2.439732	3.281964	0.876090
41	16	S	2.077841	2.919356	-0.783010
42	1	H	1.872650	2.540451	2.801090
43	1	H	3.124414	4.083380	1.118690
44	1	H	0.505784	1.056820	-1.051110

E(RB3LYP) = –1585.18980514 Hartree

Thermochemistry:	Temperature: 195.15 Kelvin	Pressure: 1.000000 Atm
Zero-point correction =	0.349264	
Thermal correction to Energy =	0.361983	
Thermal correction to Enthalpy	0.362601	
Thermal correction to Gibbs Free Energy =	0.315681	
Sum of electronic and zero-point Energies =	-1584.840541	
Sum of electronic and thermal Energies =	-1584.827822	
Sum of electronic and thermal Enthalpies =	-1584.827204	
Sum of electronic and thermal Free Energies =	-1584.874124	

Table C75. Cartesian coordinates and energies for Product **Prod–4c/Prod–4d (Trans)** found in Figure 5.19, Figure 5.21 and Table C59. Structure was optimised at the RB3LYP-GD3/6-311++G(d,p) level of theory. Energy values are reported in Hartree (a.u) units.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	3	Li	0.567860	-1.086964	-1.476169
2	3	Li	-0.779322	0.930798	-1.478578
3	6	C	-1.136872	3.503762	-0.064565
4	8	O	-1.805419	2.354330	-0.635060
5	6	C	-2.915775	2.055856	0.238790
6	6	C	-2.341513	2.237888	1.642685
7	6	C	-1.296468	3.370095	1.465044
8	1	H	-0.101194	3.473564	-0.400496
9	1	H	-1.619782	4.411594	-0.442239
10	1	H	-3.728835	2.764216	0.035629
11	1	H	-3.247621	1.041560	0.020883
12	1	H	-3.112925	2.483740	2.374190
13	1	H	-1.857301	1.310575	1.953315
14	1	H	-1.639685	4.310324	1.899866
15	1	H	-0.348069	3.110051	1.937042
16	6	C	1.125424	-3.518193	0.119998
17	8	O	1.691177	-2.426046	-0.639218
18	6	C	2.915794	-2.059231	0.032610
19	6	C	2.561006	-2.120909	1.518660
20	6	C	1.481524	-3.233465	1.593659
21	1	H	0.054341	-3.528450	-0.077728
22	1	H	1.573812	-4.455165	-0.228733
23	1	H	3.695669	-2.784983	-0.230131
24	1	H	3.201712	-1.068142	-0.316565
25	1	H	3.433122	-2.334201	2.138670
26	1	H	2.147594	-1.160467	1.830676
27	1	H	1.857370	-4.134535	2.081169
28	1	H	0.605055	-2.893453	2.146574
29	6	C	1.555325	1.186878	0.130092
30	6	C	1.380587	0.934255	-1.208480
31	6	C	2.565851	1.389612	-1.908631
32	6	C	3.553114	1.937899	-1.131699
33	16	S	3.098804	1.946710	0.544522
34	1	H	2.689878	1.308065	-2.984962
35	1	H	4.510784	2.338314	-1.435483
36	1	H	0.886092	0.979427	0.956724
37	6	C	-1.483945	-1.043202	-0.796955
38	6	C	-1.606330	-1.227298	0.572743
39	6	C	-2.823332	-1.822623	1.041891
40	6	C	-3.688266	-2.120683	0.024576
41	16	S	-2.973600	-1.661217	-1.498103
42	1	H	-0.819903	-0.931627	1.262144
43	1	H	-3.043598	-2.017178	2.085832
44	1	H	-4.668201	-2.572728	0.086884

E(RB3LYP) = –1585.18985422 Hartree

Thermochemistry:	Temperature:	195.15 Kelvin	Pressure:	1.000000 Atm
Zero-point correction =		0.349540		
Thermal correction to Energy =		0.362205		
Thermal correction to Enthalpy		0.362823		
Thermal correction to Gibbs Free Energy =		0.315786		
Sum of electronic and zero-point Energies =		-1584.840314		
Sum of electronic and thermal Energies =		-1584.827649		
Sum of electronic and thermal Enthalpies =		-1584.827031		
Sum of electronic and thermal Free Energies =		-1584.874068		

The End.